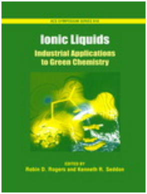

Ionic Liquids

Industrial Applications to Green Chemistry

EDITED BY

Robin D. Rogers and Kenneth R. Seddon

Ionic Liquids: Industrial Applications for Green Chemistry

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Ionic Liquids

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Foreword

The ACS Symposium Series was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of the series is to publish timely, comprehensive books developed from ACS sponsored symposia based on current scientific research. Occasion-ally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

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Preface

This book contains the key papers presented at the American Chemical Society (ACS) national meeting symposium "Green (or Greener) Industrial Applications of Ionic Liquids," held in San Diego, California, April 1–5, 2001. This symposium was the first open international meeting on the fundamentals and applications of ionic liquids (although a closed NATO–ARW meeting was held in Crete in April 2000). The sessions at the ACS symposium were the best attended at the meeting, a clear marker of the vast current interest in the industrial applications of ionic liquids. Our peak attendance was more than 275, and average attendance for the first four days was more than 180. The meeting was split into 10 sessions (Ionic Liquids in Context, Separations and Engineering, Green Synthesis, Nuclear and Electrochemistry, Ionic Liquid Systems, Properties of Ionic Liquids, Catalysis I, Catalysis II, Structure and Photochemistry, and High-Temperature and Other Systems), running from Sunday morning to Thursday afternoon; more than 60 oral presentations were delivered. Page restrictions have prevented the publication of all the presentations, but we have tried to select a representative subset of the papers. It is amazing that such a variety of topics, of such novelty and interest, could be presented when, a few years earlier, the Gordon Research Conference on molten salts died from lack of interest, and ionic liquids were considered an academic curiosity, of no practical use.

Figure 1 shows the trend in publications in this field. The recent steep rise was the reason and justification for holding the meeting and for publishing this book. We felt that a meeting that would both bring together the key players in this burgeoning area and allow the presentation of material prior to its publication would encourage the growth of this field even further. Moreover, as the growth of this area can be tied to the potential applications of ionic liquids to green industrial processes, the symposium was planned to provide a forum for the exchange of ideas between academia and industry. This element of the meeting was exceptionally successful and encouraged us to plan a second symposium at the fall 2002 ACS national meeting, held in Boston, Massachusetts, August 18–22, 2002.

The 2001 meeting would not have been successful without invaluable support from the following academic, industrial, and professional organizations. The symposium was hosted and sponsored by

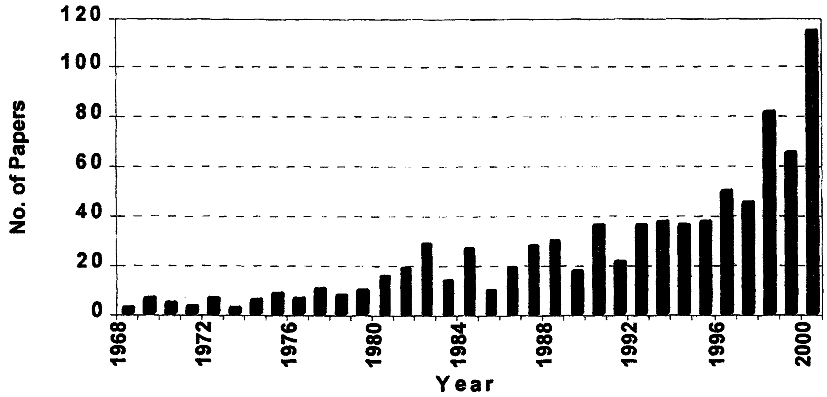

Figure 1. Publication of papers on ionic liquids and room-temperature molten salts.

two subdivisions of the ACS Industrial and Engineering Chemistry Division: Green Chemistry and Engineering, and Separation Science and Technology. Additional financial support for the symposium was received from The University of Alabama Center for Green Manufacturing, The Queen's University Ionic Liquid Laboratory (QUILL) in Belfast, the U.S. Environmental Protection Agency's Green Chemistry Program, the Green Chemistry Institute, ACROS, bp Chemical Stream, Covalent Associates, Chevron, Dow Agrosciences, Ozark Fluorine Specialties, SACHEM, Solvent Innovation, and Union Carbide. In addition, the Department of the Army, Army Research Office, sponsored the technology review, the last chapter of this book. We are indebted to these organizations and the individuals who represent them for their foresight in sponsoring this area, and we look forward to continuing to work with them as the field develops.

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Chapter 1

Green Chemistry and Ionic Liquids: Synergies and Ironies

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Ionic liquids are often portrayed as Green Solvents, however, ‘Greenness’ can only be measured in the context of the overall process. A perspective on the applications of ionic liquids in Green Chemistry, which focuses on the characteristics of ionic liquids and their contributions to Green Synthesis and Separations processes, followed by an explanation of the objectives and general organization of this book are presented.

The recent growth in interest in ionic liquids (ILs), reflected by articles in the scientific and popular press (*1*) has been driven largely by the perceived opportunities that are presented to effect improvements in industrial processes by using Green principles, driven by increased environmental awareness and the desire for increased process efficiency with associated overall cost savings (2).

The basic, fundamental concepts behind both Green Chemistry and Ionic Liquids is not new, however, the growth of interest in ILs and the influence of new minds, new approaches and enthusiasm are generating new solutions and driving changes in industrial and commercial practice, proving that Green Chemistry alternatives exist. Industrial adoption of new methods and practices is, however, ultimately going to be based on cost and demonstration of both viability and significant improvements over current practice. ***It is essential that ionic liquid processes and technologies can be shown to be better than existing methods.***

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

The work described here was presented at the ACS symposium, "Green (or Greener) Industrial Applications of Ionic Liquids" held in April 2001. The contributed chapters illustrate the diversity of research currently using ILs for Green processes, and describe some of the new applications of IL (including initial explorations of polymerization and biocatalysis) that show indications of great future potential.

Green Chemistry Approach - Process Management

The Green Chemistry approach involves taking a chemical process in a wide context - considering the life-cycle and fate of chemicals (building blocks) throughout the process. Green chemistry is not a new concept, but represents a unified effort towards environmental management of the chemical synthesis and production process, considering all aspects and trying to address waste, efficiency, and cost-benefits through reduction in divergent streams in the widest context.

Driven by the poor societal image of the chemical industry and ever increasing environmental regulations, there is a real need to take proactive steps to demonstrate that chemical technology and the chemical industry are, in the widest context, capable of providing clean efficient technology with limited environmental impact. The general perception of the chemical industry is that it has been responsible for an array of environmental and heath related problems - thalidomide, dioxins, DDT, PCBs, CFCs, and contamination and bioaccumulation of toxic, persistent, or non-biodegradable materials are examples commonly presented. The reality, often unrecognized, is that the chemical industry also underpins all of society's improvements; antibiotics, fertilizers, pesticides, polymers, and composites are some examples of the products that modern society relies upon. These perceptions, and the very real problems with production, use, and waste of undesirable products within aspects of the chemical industry (*3*) have led to a massive growth in environmental legislation and significant moves towards incremental, step-wise, and process changes within the industry.

Green Chemistry is really about re-evaluating our perspective of whole processes which center around chemical synthesis or production, using some simple and, one might say, obvious guides in order to increase overall efficiency by aiming towards elimination of waste (be that undesirable side products, energy waste, financial waste from inefficient reactions, expensive reagents, catalysts and solvents, disposal costs, etc.). Among these directors is the move to processes employing cleaner solvent solutions to reduce the reliance on VOCs, especially halogenated organic solvents. Growth of interest in ILs as solvents for chemical reactions and separations (*4*), as distinct from electrochemical

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applications has been fueled by the potential benefits that are offered by ILs as non-volatile replacements for VOCs (*5-7*).

While it is certainly true that ILs have negligible vapor pressure, and can be used as alternatives for VOCs as solvents for synthesis and separations processes (*8*), the simple replacement of one solvent with another does not necessarily make a process 'Green'. ILs are much more than just non-volatile solvents; the unique combination of properties allow new innovative chemistry, improved selectivity, and new separation and extraction procedures to be made available. These aspects will enable the development of efficient, Green processes.

Ionic Liquid Perspective on Green Chemistry

ILs have been identified as one of the new classes of solvents that offer opportunities to move away from traditional chemical processes to new, clean, Green technologies in which waste streams are minimized with the goals of atom-efficiency and resulting environmental and cost benefits.

ILs typically comprise of an organic cation and an anion (Figure 1), and have (by definition) low melting points (< 150 °C) induced largely by packing frustration of the usually asymmetric cations. Common characteristics of ILs include:

- Ionic in composition, comprising discreet, dissociated ions – though there are indications that ILs are, in many cases strong, structured liquids.
- Electrical conductivity.
- Lack of vapor pressure.
- Facile variation in properties, adding flexibility to this 'class' of solvents.
- Inherent ionic strength, though not being apparently very polar.

Favored ILs are non-volatile, often with thermal stability to over 350 °C, which can minimize solvent losses to evaporation and environmental release. Low volatility also adds a safety benefit by ensuring that the flash point for combustion is high. Chemicals can be recovered from non-volatile ILs by distillation/sublimation and pervaporation, however, non-volatility also means that ILs cannot be purified by distillation!

Among the resultant properties of ILs that distinguish them from higher temperature molten salts is the variable coordination - through hydrogen-bond donor and acceptor functions, dipole interactions, and CH-aromatic packing (which seem to be the only explanation for high solubility of benzene in many ILs) and variable co-solvent miscibility; from miscible to immiscible with polar

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solvents (i.e., water) and apolar liquids. These properties have been investigated in liquid-liquid partition and extraction studies (*5,9*), in miscibility with sc-CO_2 (*10*), and solute retention studies using liquid chromatography (*11*).

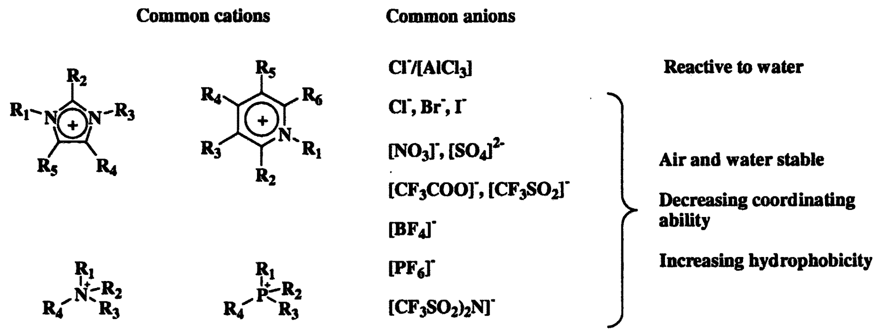

Figure 1. Representative common cations and anions used in combination to prepare ILs.

What makes a solvent 'Green' is it's use in context. None of the mentioned properties of ILs necessarily result in clean, or Green processes. Green comes from increasing the efficiency, reducing waste and losses. If an ionic liquid can contribute to this, then they can be incorporated into the Green Chemistry Tool Kit.

The potential to use the properties of ILs in order to facilitate simple product separation after catalytic reactions was recognized by Parshall (*12*) nearly thirty years ago, '*A major problem in homogeneous catalysis is the separation of products from the catalyst...An approach that seems under utilized is the use of molten salts as stable, non-volatile solvents from which organic products are readily separated by distillation...A substantial advantage of the molten salt medium, however, is that the product may be separated by decantation or simple distillation*'. Novelty, combined with the limited available range of low melting molten salts, were significant barriers to general acceptance and utilization of ILs or low temperature molten salts.

The growth in both interest and the accessible variety of ILs stems from electrochemical studies on molten salts and a desire to reduce operating temperature utilizing low melting organic salts as alternatives to high temperature molten salts as liquid ionic electrolytes. Electrochemical studies in ILs continues as a fascinating and important aspect of research, producing applications in capacitors, batteries, electroplating, dissolution, and electrosynthesis (*13*). From this work developed the realization that these same

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highly reactive, chloroaluminate ILs could function as both solvent *and* catalyst for various Lewis acid catalyzed reactions in place of solid heterogeneous catalysts. The important observations made about the behavior of ILs as solvents remains the driving force for their use in a Green Chemistry approach.

Early chemical applications of IL focussed on the properties of the ILs that gave process improvements; greater reactivity, ease of product separation with reduced down-stream processing, and stabilization of catalysts; all 'Green' features of the overall process. As examples Friedel-Crafts alkylations and acylations (*14*), alkylation of olefins (*15*), and nickel-catalyzed olefin dimerization reactions (*16*) all utilized IL systems as both solvent and catalyst for the chemical transformations and took advantage of poor product solubility to facilitate clean separations which could improve process and separation efficiency. From electrochemical studies, new IL classes have been developed, opening access to air/water stable ILs containing a wide range of anions, including nitrate, triflate, tetrafluoroborate and hexafluorophosphate.

Other ILs and other uses of materials we would now call ILs were known, and the importance of this work as a foundation for modern IL chemistry has to be recognized; liquid examples of phase transfer catalysts (*17*), typically tetraalkylphosphonium salts, are of course ILs. Ammonium and phosphonium salt 'melts' have been used as catalyst solvents for industrial hydroformylation reactions (*18*), etc. The extensive body of research on liquid-liquid clathrates and glass forming organic salts has yet to be effectively incorporated into the overview of ILs. Finally, the first recorded true ionic liquid, ethylammonium nitrate (*19*), has been widely used in the study of protein folding and surfactant structuring (*20*). Applications of other ILs in biochemistry and biocatalysis are now beginning to emerge.

The requirements for an ideal solvent include; low toxicity, non-flammability, availability at low cost, high capacity for solutes, high selectivity for solutes, low selectivity for carriers, inert to materials, moderate interfacial tension, and compatibility. ILs can meet some of these requirements now, with expectations to address the remaining issues: cost, stability, toxicity and environmental impact, corrosion, and recycling.

ILs represent a class of solvents that may allow both efficient, controlled chemical reactions *and* selective extractions of products and regeneration of the solvent systems. Ready modification of the solvent properties of an ionic liquid enable tuning of solvent parameters, which represents the greatest opportunity to generate optimized solvents for processes and syntheses. One should note that many projected applications promote the use of ILs as replacements for VOCs. However, simple direct replacement of VOCs with an IL does not address the needs to then dispose of used and possibly contaminated ILs.

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ILs as Solvents for Chemical Reactions

Modern development of ILs as solvents for chemical reactions (5,6), particularly for catalysis (7), has been recently reviewed. Earlier work on chemical applications of low temperature molten salt systems up to the mid-1980s have also been comprehensively reviewed by Pagni (*21*).

Early work focussed primarily on hydrocarbon transformations (of particular relevance to the petrochemical industries), principally using acidic tetrachloroaluminate(III) ILs. Driving forces for using ILs as catalysts/solvents for chemistry were increased reactivity, ease of product separation, and reduced down-stream processing. In these systems, in many cases, the products fortuitously are less soluble in the ILs than the reagents, enabling control of reactivity and allowing for simple product separation by decanting or gravity separation. By applying enhanced, catalytic selective reactivity and separation principles, enhanced isolated yields of products, and IL and reagent recycling and regeneration are possible.

The diversity of current studies has increased dramatically, whereas even recent reviews (*5-7*) were only able to describe a relatively small subset of reactions that had been carried out in IL systems – Friedel-Crafts chemistry, alkylations, transition metal catalyzed oligomerization, dimerization and polymerization of olefins, and C-C bond forming reactions – current research areas are starting to address chemical applications in a much wider context. As ILs cease to be novel materials, and become more widely accepted, then this trend is set to continue and will lead to full-scale production processes.

Among the new areas under study, that are represented by contributions to this symposium proceedings, include developments in transition metal catalyzed C-C bond forming and hydroformylation reactions, olefin oligomerization, hydrosilylations, catalytic oxidation and nitration, superoxide chemistry, and the role of IL acidity in H-transfer processes. New applications of ILs as solvents in pharmaceutical and fine chemical synthesis, for biochemical transformations, chemistry of sugars for the utilization of biomass, and radical polymerization are described, and show how ILs research is maturing and opening into new fields.

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IL in Clean Separations

Incremental changes in chemical transformations have required often fundamental changes in the separation and extractions processes. Applications of ILs are no different, the non-volatility of many ILs in particular presenting both a new set of challenges and opportunities in extraction to, and from, ILs. Separation processes are of interest for isolation of products from reactions. Potential applications using IL separation processes include primary metal extractions, refining and recovery of materials in the nuclear industry, and in the preparation of selective liquid membranes and sensors. Physical chemistry and engineering studies reveal both opportunities to exploit the properties of ILs in new uses and also give important insights into IL structure and inter-ion interactions. Recent investigations have included IL-liquid (*9*), IL-sc-CO_2 (*10*), and IL-gas (22) systems including distillation and membrane separation approaches.

The development of new ILs and the study of their physical properties are important in order to obtain sufficient information to predict properties and solvent characteristics (*23,24*). In particular, structural results can be used to develop selective dissolution and extraction/partitioning schemes. Part of the Green ensemble is the mechanism to transport a chemical from A to B with lowest energy/effort costs. A necessary, but sometimes onerous, part of this is the generation of high quality, reproducible physical data, identifying how solutes interact, and partition between ILs and other solvents (*25*). Although ILs contain only dissociated ionic species, in many cases they are less polar than water and many salts are poorly soluble in the ILs, showing a marked preference for aqueous phases.

For hydrophobic ILs, IL-water partitioning have been compared to the traditional partitioning measure, the octanol-water partition. This comparison has proved to be extremely valuable in quantifying the properties of ILs. Though it must be noted that ILs are very different to octanol in terms of the solvent-solute contributions to miscibility or solubility. In some cases, even hydrophobic ILs can become totally miscible with water (*26*).It is worth noting that octanol-water partitions are widely used as a general measure of solvophilicity, biotoxicity, etc. Toxicity studies on ILs and IL-like materials are rare (*27*), and do not necessarily give consistent conclusions. Future developments in these fields are likely to come from an understanding of ILs, their solvation and solvent properties, and comparative studies of the nature and reactivity of systems as a function of the ionic liquid environment, for example, comparing ILs containing ***structure-making*** and ***structure-breaking*** anions.

Among the papers presented at the symposium, are investigations of physical and rheological characterization of ILs, photochemistry, liquid-liquid equilibrium, gas solubility, actinide chemistry and separations, gas separations using supported IL membranes, and solvent extraction processes for nuclear, heavy metal, and mining applications. These examples show ILs not only replacing VOCs, but also utilizing the properties of the ILs to enhance the performance of the system (for extraction, separation, reactivity, and reduced catalyst leaching).

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Organization of Chapters

Chapters submitted for this book are based on papers from the symposium "Green (or Greener) Industrial Applications of Ionic Liquids" at the ACS National Meeting, San Diego, CA April 2001. One of the most fascinating features of this meeting was the level of interest generated in IL research and applications. At a recent NATO sponsored Advanced Research Workshop (*1a*), the organizers had struggled to commit 50 speakers, whereas only one year later, not only did the symposium attracted over 80 oral presentations, but attendance in the sessions over the entire week was consistently high, and on occasions left 'standing room only': over 275 people attended the opening session. This level of interest is reflected in the diversity of papers presented in this volume, covering Green applications of ILs in synthesis, catalysis, bio-catalysis, and all aspects of the processes around a central synthetic step, including separations, extraction, and physical and engineering properties.

A perspective on the origins and development of room temperature ILs from the work at the Air Force Academy is given by Wilkes which describes the approach made to design new low temperature molten salt electrolytes. The path from the initial research, and researchers, through to current day ILs applications is shown.

The criteria used to define Green Chemistry and consideration of the position of ILs as Green solvents or as components of Green processes is made by Nelson. Structural, chemical, and engineering properties of IL are discussed in contributions from Johnson (effects of cations on electrochemical and chemical properties of ILs), Rogers (properties of ILs relevant to solvent extraction), Gordon (photochemical approaches to determining solvent properties of ILs), Rogers (solvatochromic parameters for ILs), Brennecke (gas solubilities in [C_4mim][PF_6]), Martin (structure relationships), and Hardacre (X-ray reflectivity and SAXS studies of IL structure).

Development of Green processes require fundamentally more than just an efficient reaction; clean, efficient methods to recover products or reagents are also needed. The design of new ILs is described by Davis (Task Specific Ionic Liquids) and Costa (preparation of new ILs for use in actinide chemistry), while Matthews (superoxide ion generation and electrochemistry, for waste oxidation) and Bartsch (enhanced solvent extraction with crown ether complexants) discuss applications of ILs in separations and clean-up. Noble describes IL-engineered membranes for gas separation and Dai shows how silica-aerogels can be prepared in IL solvents to enable fabrication of stable mesoscopic materials.

The use of ILs as solvents for clean synthetic chemistry is reviewed by Earle, and chemistry in ILs and on heterogeneous metal oxide surfaces is compared by Pagni. Specific developments, using ILs solvents for catalytic transformations with applications ranging from fine chemicals to industrial

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petrochemical applications are described by Welton (Pd-catalyzed C-C coupling reactions), Wasserscheid (Pt- and Rh-catalyzed hydroformylation), Ranwell (catalyzed olefin oligomerization), Vaultier (transition metal catalyzed hydrosilylation and hydroboration of alkynes), Abu-Omar (catalytic oxidation), and Handy (transition metal catalyzed nitration). McCluskey describes improvements to allylation reactions using organostannane reagents with applications in pharmaceutical synthesis and use of ILs as additives for primary recovery of copper from chalocopyrite ores, while Moens presents experiment to utilize ILs to access biorenewable chemical sources.

Initial results from radical polymerization reactions are reported by Haddleton, May, and Brazel. Their results indicate that, compared to the reactions in conventional solvents, polymers with much higher molecular weights can be obtained and that the polymerization reactions can be controlled by matching the IL solvent to monomer and polymer solubility.

Enzymic processes in solvents of high ionic strength, such as ILs, seem to be unlikely combinations. Chapters from Lye (biocatalysis) and Lazlo (chymotrypsin catalyzed transesterifications in IL/sc-CO_2), however, establish that ILs can indeed replace organic solvents in bioconversion processes.

In addition to the oral and poster presentations, the symposium also featured a technology review session, supported by the Army Office of Research, to explore the current status of IL technologies and highlight specific areas of potential for the development of new, improved technologies for synthesis, separations, electrochemistry and preparation of new materials and devices. The outcomes and recommendations from this review are reported in the last chapter of this book.

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Summary

Current developments in IL science and technology provide a portfolio of solvents ranging in properties from hydrophilic to hydrophobic, acidic to basic, variable lipophilicity and redox properties, and containing catalytically active, or task-specific functionality. The range of available and potential ILs may appear overwhelming, but allows the scientist or engineer to develop new processes, selecting an IL based on a subset of desired characteristics.

The expectation that real benefits in technology will arise from IL research and the development of new processes is high, but there is a need for further work in order to demonstrate the credibility of IL-based processes as viable Green Technology. In particular, comprehensive toxicity studies, physical and chemical property collation and dissemination, and realistic comparisons to traditional systems are needed. The current lack of relevant toxicity and BOD data currently undermines all claims that ILs are nontoxic (and, we might comment, appears to indicate a lack of confidence in ILs), full life-cycle analysis and regulatory issues have to be tackled immediately. These are functions that should be addressed by the industries expecting to benefit from the production and sales of ILs.

In using ILs as solvents for reactive chemistry, some reactions are demonstrably better than in other solvents (the Heck reaction (*28*) can be highlighted as one example) and many products can be easily extracted or separated from ILs. But, many compounds are exceptionally and intractably soluble in ILs: aldehydes, ketones, and other dipolar organic compounds in particular appear to be very difficult to remove by either extraction or distillation and new approaches to separation have to be applied.

In cases where reactions are enhanced, extraction may be easily facilitated and the ILs reused. These features make the ILs good candidates as solvents for novel Green manufacturing processes (in examples such as Diafasol, and BP's IL Friedel-Crafts alkylation technology, as upgrades to existing plants). Catalysis, polymerizations, organic synthesis, and enzymatic processes all have been demonstrated with excellent results. Methodologies to utilize ILs in extraction, separation, and purification processes are showing promise. Much of the chemistry/extraction technology investigated is not totally new. Indeed the approach taken in many cases has been to revisit existing reactions and examine whether the use of ILs can give synthetic improvements.

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It is ironic that IL are being touted for Green Chemistry, and yet so little is known about their toxicology and long term effects of their use. In addition, many examples are now appearing of novel chemistry being conducted in an IL solvent, but with a VOC being used to separate reaction products from the IL! [*29*] It is clear that while the new chemistry being developed in IL is exciting, many are losing sight of the 'Green' goals and falling back on old habits in synthetic chemistry. While it is true that incremental improvement is good, it is hoped that by focusing on a Green agenda, new technologies can be developed which truly are not only better technologically, but cleaner, cheaper, and safer as well. One would anticipate that additional benefits of R&D under such a Green banner would include a workforce trained to think, plan, and solve problems in a manner which emphasizes economically, environmentally, and socially sustainable technologies.

ILs are not new, not 'Green' in full context of limited data we have at present, but do offer great opportunities to be used in Green processes AND to provide radically new process solutions. In acknowledgement of the great volume of work associated with ILs (molten salts, IL electrochemistry, catalysis, reactions separations, materials science, organic and inorganic glass formation, liquid clathrates, liquid phase transfer chemistry, liquid surfactants, biochemistry, etc.) that has been used as a basis to advance our current understanding we should remember the words used by Sir Isaac Newton (*30*), '*If*

I have seen further it is by standing on ye shoulders of Giants' and look to exciting future developments from the use of ILs in many new applications.

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Chapter 2

Neoteric Solvents: An Examination of Their Industrial Attractiveness

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The prime driving force for the early adoption of a new technology in the manufacture of fine and speciality chemicals is the delivery of a new or significantly improved product to the market. Next is a substantial reduction in the cost or complexity of an existing process. The work published to date on room temperature ionic liquids shows only a small number of instances of attractive new chemistry which could form the basis of better market place performance. Compared with supercritical carbon dioxide, the technology of ionic liquids is at an early stage of development.

Sustainability and Chemical Technology

The transition to a stable sustainable global economy at a time of rampant global warming poses many challenges for technology and science. The most pressing are: the development and adoption of renewable energy to replace the reliance on fossil fuels, systems for purification and distribution of water, and creating the basis for systems of food production and distribution which preserve and

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

improve topsoil and stocks of flora and fauna. Given the scientific advances of the last century in materials and biotechnology, there are no doubts that the technical problems are solvable. It is less clear that the political will exists to implement solutions.

New industrial chemical technologies - for transformation and separation - are central to achieving sustainability. They will have to meet high standards in terms of atom efficiency, low waste production, reduction in hazard, and use of renewable or recycled feedstocks. The principles of Green Chemistry, as listed by Warner and Anastas *(1)*, provide a first set of guidelines for the criteria against which the environmental profile of new technologies can be measured.

New solvent systems are prominent among the academic work done under the banner of Green Chemistry. As a result, they are among the most advanced of the new technology options currently offered to industry as candidates for future development. The environmental driver to reduce reliance on volatile organic compounds is intuitively attractive, and is reinforced by the prospect of ever more stringent legislation.

The aim of this paper is to examine the status of three embryonic solvent technologies against the criteria which would make an industrial concern commit resource to their development for potential use as new reaction media for chemicals manufacturing. This means asking three questions:

- what added value can be achieved by switching to one of the solvents?
- are the environmental and other safety criteria acceptable?
- are all the elements of the technology in place or under serious development?

Scope and Sources

The paper is confined to three solvent systems: ionic liquids, supercritical carbon dioxide, and fluorous solvents. Three central processes for chemical transformation are examined: hydrogenation, oxidation, and carbon-carbon bond formation. It is based on the academic and patent literature through to February 2001. There is thus implicit in the approach the limitation that some recent work on these solvents will not have been published while patenting is in progress, and that the view is therefore incomplete. Much important industrially sponsored work will not be captured because of delays in publication.

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The technologies are addressed from the standpoint of the fine and speciality chemicals sectors. These sectors produce high value products which are either end-use chemicals or intermediates for pharmaceuticals, fragrance, agrichemicals, special polymers and the like, selling on purity (fine) or effect (speciality). Individual product tonnages are small, a few hundred or thousand tonnes per annum, and manufacturing campaigns tend to be short. At the higher tonnage end there are dedicated continuous plant, but in general the norm is small scale batch processes in plant which is flexible enough to handle several different reactions, with minimum downtime for cleaning in between. Speed is essential for these companies; new business depends on winning contracts from larger companies, and new processes must be developed and implemented in matters of weeks or months. Quality too is critical to all aspects of operation; many processes will operate to the standards of Good Manufacturing Practice, an essential if materials are to go into health and safety trials.

This sector is seen as one of the more profitable within chemicals manufacturing, not least because it services the rapidly expanding market for stereochemically pure pharmaceuticals. Its needs have been assessed in a number of recent formal government and industry studies, such as Foresight (UK) *(2)*, Vision 2020 (USA) *(3)*, and OECD *(4)*. The author has also drawn on recent reports and workshops from European organisations, which in different ways have illuminated the opportunities seen by chemicals companies. These include NICE (Network for Industrial Catalysis in Europe), SOCSA (Speciality Organic Chemicals Suppliers Association), The Institute of Applied Catalysis (UK), NIOK and VIRAN (the Dutch academic and industrial catalysis networks). The needs of the sector are also articulated at Chemspec, the annual industry conference.

Emergent Manufacturing Technologies in the Chemicals Industry

Manufacturing technologies mature through the combined experience of users, suppliers and regulators. (Figure 1) In the early stages, laboratory studies are scaled up to demonstrator projects aimed at proof of concept, often with significant government funding. This will be succeeded by custom developments. It is only after many years, when the materials and knowhow have been widely disseminated, that a technology becomes one of the standard choices for use by an industry sector. A relevant example is provided by the application of zeolites as catalysts for the manufacture of intermediates and speciality chemicals. This is still not fully established as a technology even after some fifteen years of custom developments, despite a strong supply situation and many thousands of chemists and chemical engineers trained in zeolite research.

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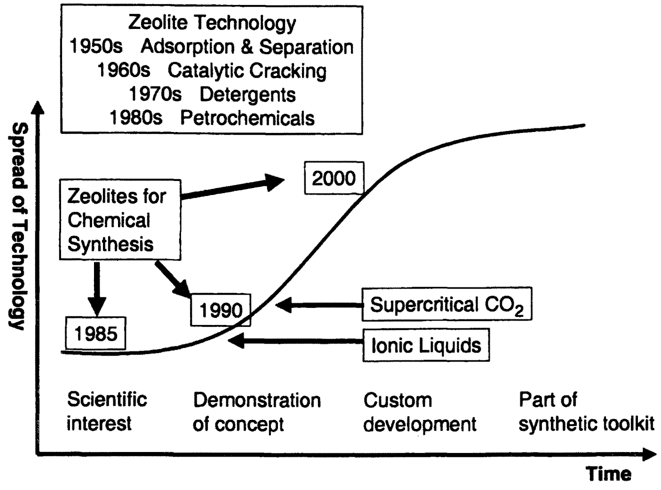
Zeolite Technology
1950s Adsorption & Separation
1960s Catalytic Cracking
1970s Detergents
1980s Petrochemicals
Zeolites for Chemical Synthesis
2000
1990
1985
Supercritical CO_2
Ionic Liquids
Spread of Technology
Scientific interest
Demonstration of concept
Custom development
Part of synthetic toolkit
Time

Figure 1. Evolution of manufacturing technologies

New solvents are very much moving from the status of scientific interest into the demonstrator phase. The challenge for the research communities working on them is how to accelerate their progress to establishment as robust technologies. The research strategy must be based on an understanding the factors which encourage industry to explore the possibilities on offer.

The single most important driver which makes a new technology attractive is the possibility of a product benefit: obtaining competitive advantage in the market through a new product, or through a product of significantly improved quality (such as much higher compositional or stereochemical purity). (Figure 2) Second would be major process simplification: a new reaction which reduces manufacturing steps, or which eliminates the need for separations. Cost improvements would be third. New chemistry is essential to providing such advantages. Straight replacement of a solvent, without new chemistry, is unlikely to be attractive as an investment option, unless the whole industry is under notice of legislation or stakeholder pressure which affect all companies equally. This is unlikely in the short term.

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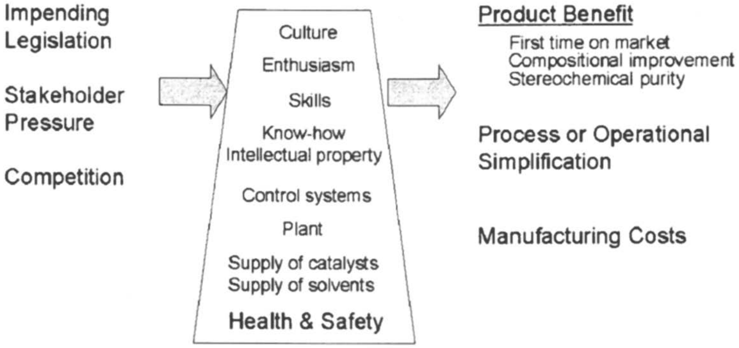
Impending Legislation
Stakeholder Pressure
Competition
Culture
Enthusiasm
Skills
Know-how
Intellectual property
Control systems
Plant
Supply of catalysts
Supply of solvents
Health & Safety
Product Benefit
First time on market
Compositional improvement
Stereochemical purity
Process or Operational Simplification
Manufacturing Costs

Figure 2. Schematic view of drivers and checkpoints for new technology

In the very early stages of creating a new technology, best industrial practice examines primarily the professional and personal qualities of the academics or other researchers driving the inventions. *(5)* After seeing a promise of new chemistry, however, and as the area matures towards demonstrator projects, the industrialist will be looking for qualitative information to assess the technical and commercial risks inherent in the emergent technology. Relevant quantitative data first surfaces from the demonstrator projects.

First will be health and safety, an assessment of the environmental and human hazards associated with the chemicals in manufacture, use and disposal.

Next will be supply. Assurance is needed that solvents and catalysts can be manufactured to the necessary specifications, and that supplies of sufficient quality are likely to be maintained. This is especially important if the end-product is intended for pharmaceutical or agrichemical use, and the manufacturing routes are subject to the requirements of Good Manufacturing Practice. A strong supplier base is also a good source of process know-how.

Concerns must be satisfied about whether special plant or equipment is needed, or special materials of construction. Perhaps of greater significance will be whether special control systems are needed to maintain the process within required boundaries. The robustness of the process technology, the sensitivity of performance to small variations in temperature, pressure or the presence of impurities will be important considerations.

Ownership and licensing of intellectual property will certainly be an issue. The prime concern will be to establish either that the technology is free of patent restrictions, or that a licence can be obtained at reasonable cost. The possibility of obtaining patent protection for the new developments needed to commercialise the process will also be addressed. Current developments in patent law, especially the likelihood of compulsory licensing, are rapidly changing the commercial approaches to obtaining value from patented processes.

The manager will judge whether the new technology requires skills which are different from the traditional base of his company, and what must be done to acquire them. The attractiveness of a technology is thus greatly enhanced if there is a strong associated base of academic expertise, and if it is used in other manufacturing industries. Process workers and other staff will need to be trained in the new technology. Undoubtedly the fastest way to gain expertise is to hire it from a company using similar technology, even in a different industry, or from a university. The truly careful manager will also seek to establish what sources of help for troubleshooting will be available when, not if, the technology experiences problems.

Lastly, well outside the technical sphere, will come an assessment of whether the technological thrust is in tune with the company culture and with its state of enthusiasm for innovation. Timing is everything in innovation, as many examples show, not least the failure of Xerox to develop the mouse and Graphical User Interface for personal computers.

Fluorous solvents

The attraction of fluorous solvents, first publicised by Horvath *(6)*, is the potential to exploit a temperature dependent phase separation: the reaction medium containing a catalyst is a single phase at elevated temperature but on reducing the temperature product and catalyst are in distinct phases, allowing separation and recycle. A further attraction is the high solubility of diatomic gases, which can assist mass transfer in gas-liquid reactions. As generally practised, the catalyst is intended to remain in the fluorous phase after phase separation. This brings a requirement for special catalysts, metal complexes whose ligands terminate in long perfluorinated alkyl chains. Commercialisable synthetic routes to these catalysts have not been reported.

Reactions demonstrated in fluorous solvents include hydroformylation *(7)*, hydrogenation *(8)*, Heck coupling *(9)* and hydrosilylation *(10)*. In general the fluorinated catalytic complexes show only similar reactivity and selectivity to

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conventional catalysts in conventional solvents. Hydroformylation of 1-decene, for example, gives normal/branched product ratios in the range 2 to 3 *(7)*. Ligand leaching appears to be a problem everywhere, with consequent problems of managing catalyst stability and performance during recycle and reuse.

Perfluorinated hydrocarbon solvents are likely to be expensive. Current industrial uses are all small scale, as special lubricants or in medical devices. Prices are accordingly high, perhaps a hundred times the cost of hydrocarbon solvents.

Based on the foregoing analysis, there is little about perfluorinated solvents that is technically or commercially encouraging. Their status as environmentally attractive options must also be re-examined. EPA estimates of Global Warming Potential rank perfluorohydrocarbons among the most pernicious of greenhouse gases due to their long lifetime in the atmosphere.

Table I. Environmental profiles of greenhouse gases

	Global Warming Potential	*Atmospheric Lifetime (yrs)*
Carbon Dioxide	1	
Methane	21	12.2
Perfluorohexane	7400	3200
Sulphur hexafluoride	23900	3200

SOURCE: EPA Website

It is hard to envisage that a large widespread manufacturing technology based on the use of highly fluorinated solvents will emerge within the next century.

Supercritical Carbon Dioxide

The literature on supercritical carbon dioxide contains examples of chemical reactions which potentially offer advantages over current best industrial practice.

Hydrogenation in supercritical carbon dioxide is potentially facile, because of the excellent miscibility of hydrogen and substrate in the supercritical medium, and has been extensively studied. Homogeneously catalysed enantiomeric reduction of amines is reported by Leitner, with a convincing demonstration of catalyst recycle *(11)*. Equally promising is a continuous heterogeneous process reported and patented by Poliakoff, using modified Degussa catalysts *(12)*; in this system

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the regioselectivity for aromatic or sidechain reduction can be controlled by adjusting temperature and pressure.

High activity and product selectivity have been demonstrated in the laboratory for the hydroformylation of 1-octene, using rhodium catalysts. Leitner describes both very productive and very enantioselective homogeneously-catalysed batch reactions *(13)*. Poliakoff's continuous laboratory process using a heterogeneous catalyst gives almost exclusively the more valuable linear isomer *(14)*.

Continuous acid catalysed alkylation of anisole promises an alternative route to Friedel Crafts chemistry (15); the use of an alkene as alkylating agent is preferable to the conventional halide. However it must be noted that anisole is an activated substrate, so there is still much to be demonstrated before an attractive process emerges. Heck coupling using conventional catalysts is so far relatively unsuccessful (16), highly reactive aryl iodide reagents giving only low yields.

It is observed that the most successful processes use catalysts which have been tailored or otherwise modified to make them compatible with the supercritical fluid. For homogeneous catalysts, ligand design principles have mainly been based on fluorinated sidechains, the so-called "ponytails", as a way of increasing catalyst solubility. How heterogeneous catalysts can best be modified is not fully reported, but it is significant that at least one catalyst manufacturer, Degussa, appears to have addressed this problem with some success *(12)*.

In other industries, large-scale working with supercritical carbon dioxide is most prominently used for the extraction of natural products, such as caffeine from coffee. There is also an extensive and growing technology associated with the use of supercritical carbon dioxide as the mobile phase in chromatography; transfer of skills and adaptation of equipment from the chromatographic application have helped the development of research into process chemistries. Other applications being researched include: fibre dyeing, fibre impregnation (e.g. with biocides) and dry cleaning. Du Pont has announced a major investment in a polymerisation plant using supercritical fluids.

Supply of carbon dioxide is not a problem, being assured by industrial gas companies like Air Products. International engineering companies such as Kobe Steel are heavily committed to the development of plant for extraction and the like, and are involved in new applications. By implication, robust technologies are being used profitably, and there is a pool of proven engineering principles for working with supercritical solvents, and considerable industrial know-how.

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The physics and chemistry of supercritical fluids have attracted considerable interest in the academic community, in both science and engineering departments *(17)*. Academics have addressed the challenge of developing a theoretical understanding of an unusual form of matter, and applying the principles to application. Businesses investing in supercritical fluid technology will find that there is a large public knowledge base, the promise of knowledgeable recruits, and the potential to find independent advice and support for troubleshooting.

Many of the preconditions have thus been met to persuade industrialists to invest in supercritical fluid technology for chemicals manufacture. Much remains to be learned, especially in relation to the economics of the system (which is reliant on plant capable of handling the pressure) and perhaps more critically on the feasibility of process control, since the properties of supercritical fluids are very sensitive to composition, especially in the regions near the critical phase boundary. The initiative of Thomas Swan, a small privately-owned British speciality chemical manufacturer, to build a multipurpose plant should clarify these questions, at least for continuous processes of hydrogenation, alkylation, etherification and hydroformylation based on the work of the Poliakoff group at Nottingham University. Engineering is being provided by the Swedish company Chematur, and catalyst technology by Degussa. Commissioning of the project is scheduled for the second half of 2001. It is instructive that a privately owned company will accept the level of risk involved in such a venture.

Room Temperature Ionic Liquids

Ionic liquids (RTILs) comprise a potentially vast, essentially unlimited, set of liquids sharing the central intriguing property of having no vapour under normal conditions. Knowledge of their chemical and physical properties is limited to a very small subset involving cations and anions selected by the research community to provide spreads of hydophobicity/hydrophilicity and acidity/basicity. Predictions about their utility must be tempered by the realisation that the liquids ultimately commercialised may be very different from the systems presently under laboratory investigation.

In the short time since research on ionic liquids became fashionable, nearly 20 different organic reactions have been investigated (Table II), with a strong focus on carbon-carbon bond formation and on hydrogenation. The list increases almost weekly. The information in most of these reports suffices to demonstrate the possibility of the reactions occurring in RTILs: in a few cases is there is a glimmer of process possibilities better than current practice.

Table II. Reactions reported in ionic liquids

Reaction	*No. papers*	*Reaction*	*No. papers*
Allylation	1	Trost-Tsuji Coupling	1
Aryl Coupling	1	Cracking	1
Alkylation	4	Hydrogenation	8
Acylation	2	Oxidation	1
Heck Coupling	5	Epoxidation	1
Oligomerisation	11	Diels Alder Addition	3
Suzuki Cross Coupling	1	Living Radical Polymerisation	1
Claisen Rearrangement	1	Enzymatic Lipolysis	2

Hydrogenation

Hydrogenation reactions in ionic liquids can use metal-phosphine catalysts like those used in conventional solvents, with similar results: Rh-BINAP can be used for asymmetric hydrogenation *(18)*; rhodium PPh_3 systems can be used with undetectable leaching of metal *(19)*. Exceptional chemistry is not yet reported, but there may be general processing advantages *(20)*: reaction rates are higher than in conventional solvents, and the products, generally less polar than the reactants, may be separated by vacuum distillation or decantation.

C-C Bond Formation

Ionic liquids may offer advantages for Heck couplings *(21)*. The reaction of aryl halides with alkenes in the presence of palladium salts is widely used in industry: the palladium is recovered but not directly reused; ligands may be lost altogether. Studies in different ionic liquids have separately shown that catalyst recycle is possible (in $bmimPF_6$) *(22)*, that the deactivation of the catalyst to palladium metal is inhibited (in Bu_4NBr) *(23)*, that benzoyl chloride (rather than bromide) can be used *(23)*, and that reaction can even be achieved with benzoic anhydride *(22)*. Combining these advantages in a single system would create a significant improvement.

Hydroformylation of terminal alkenes works well in ionic liquids, giving very high yields of the desirable linear isomer. Vacuum distillation has been used to separate the aldehydic products, utilising the absence of solvent vapour *(20, 24)*.

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The early experience of BP and IFP using chloroaluminate liquids shows conclusively that alkylation of aromatics or olefins is technically feasible where the alkylating agent is an olefin; product separation by decantation is facile, and the catalytic ionic liquid can be recycled: accumulation of polymeric by-products may be a problem *(25)*. Alkylation and acylation with alkyl or acyl chlorides introduces HCl, which is hard to separate from the catalyst. For acylation, formation of stable complexes between products and $AlCl_3$ is a major stumbling block *(26)* to a successful acylation process, as is the facile polysubstitution of reactive substrates. No new selectivities result for aromatic substitution, nor can unreactive arenes can be alkylated or acylated.

Oxidation

Ionic liquids have a high stability towards oxidation *(20)*. The relative lack of reports of oxidation reactions is therefore surprising, and is unlikely to be a persistent feature of the field. Haworth has shown that with suitable nickel catalysts molecular oxygen can convert an aromatic aldehyde to the carboxylic acid *(27)*. Jacobsen's catalyst can be used to epoxidise olefins with high levels of enantioselectivity; hypochlorite is the oxidant *(28)*.

Comments on RTILs as technology

The range of chemistry demonstrated in room temperature ionic liquids is considerable wider than fluorous solvents or supercritical carbon dioxide, and includes some effects of potential commercial interest.*(29)* Separation of the product from the reaction mixture will be a key challenge in converting this promise into real processes; many early studies destroyed the RTIL during product recovery. Decantation is possible for non-polar products which form a separate liquid phase with the RTIL. Vacuum distillation has been shown to work for thermally stable products. Two phase systems employing a second solvent hold promise, but in many laboratory studies the second phase has been a conventional organic solvent, which rather defeats the environmental purpose of using RTILs. Using supercritical CO_2 as the second phase is a very recent and promising option *(30)*. There are verbal reports of product crystallisation, but no published results.

The emergence of strong university centers, at RWTH Aachen, QUILL at Queen's University Belfast, and at the Centre for Green Manufacturing at the University of Alabama, all with strong technical support from industry, should nucleate further investment in RTIL research, and broaden the applicational base.

To say there is as yet little technology aimed at applications other than chemicals production merely emphasises how recently this class of material has become available. More surprising is the relative lack of interest in the physics and physical chemistry of room temperature ionic liquids. The early work of Wilkes apart, only recently have the first descriptions of simple physical properties, such as gas solubilities and liquid miscibilities been published *(20)*. Equally recent are structural studies which begin to assess distributions of cations and anions in pure liquids. Little work yet extrapolates theory from well known related topics, e.g. the physics of surfactant phases, or the crystal engineering of organic solids.

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A supply position is emerging. Several companies offer trial materials in technical grades and research grades. Having independently produced materials available is a spur to the applied research effort; it also implies that manufacturing routes for the liquids will be improved. But here is a great danger for the growing field. Much anecdotal evidence about ionic liquids, and some published work, implies that physical and chemical properties are very sensitive functions of composition. While the academic community is for very good reason trying to work with and define the chemistry of very pure compounds, future technology is likely to rely on materials containing impurities, albeit known impurities at consistent levels. This is especially true if liquids are to be re-used or recycled. It will be a real test of the growing ionic liquids community to handle this duality with sensitivity, understanding and mutual respect for the two positions.

The implications of compositional flexibility of RTIL systems raise more fundamental questions for commercialisation.

- The concept of "solvent tunability" is a great sales pitch, but processes consistency demands regions of stable solvent properties. Major challenges for process control will result if the change of properties is not a smooth function of composition.
- Equally daunting for the industrialist is the idea that, if a process works well with one liquid composition, it will be possible to find many other compositions with the same properties; developing a patent strategy under these circumstances will require considerable ingenuity.
- Lastly, the registration of new materials under European Health and Safety legislation is based upon compositions: the financial consequences of having to test and register each new RTIL composition, including subtle variants, would indeed be a severe obstacle to widespread commercialisation. Normally such costs are borne by the individual companies seeking first registration. RTIL manufacturers taking this step would, it is assumed, seek to recover registration costs in the price charged for the materials.

Concluding Comments

These last remarks are aimed mainly at ionic liquids. There has indeed been a very rapid growth of interest in chemistry in RTIL solvents, but what has been published to date is mostly the demonstration of known chemistries, using well known reactions, facile substrates and reactive agents. With the possible exception of hydroformylation, there is no compelling evidence for really new chemistry. Given the uncertainties in other aspects of the ionic liquids prototechnology, the product or process improvements deliverable from current public knowledge do not constitute sufficient grounds for a drive for commercialisation.

Processes using supercritical fluids for polymer manufacture are already being built, and it seems impossible that the technology will not spread in time to other areas of chemicals manufacturing, with decisions based on simple considerations of economics. The future for fluorus solvents looks bleak, given their environmental profile, but the catalysts with fluorinated ligands generated through research in this area look to have considerable potential in supercritical fluid reactions.

Industrialists frequently complain about the lack of industrial relevance in new chemistry produced by academics. The problems arise in no small measure from the industrialists themselves, and their ineffective communication of the key needs of new process development. It is also true, however, that academics need to listen better to industrialists, as well as promoting their own ideas.

It is particularly recommended that for a novel unproven technology like ionic liquids, industrial enthusiasm is most easily kindled if the technology offers chemistry which is not available by other means, or seeks to replace chemistry with serious defects. Examples of some such needs, collated from information presented at open meetings in Europe, are:

- selective oxidation and ammoxidation, with high conversions
- direct aromatic hydroxylation
- Friedel Crafts acylation of unreactive arenes with carboxylic acids, avoiding polysubstituted products
- Mild selective hydrogenation, e.g. of carboxylates, amides, avoiding $LiAlH_4$ and other hydrides, or using low pressure hydrogen
- Wittig type chemistry (C=O to $C=CR_2$) avoiding phosphine oxide waste
- Stereoselective aromatic hydrogenation
- One pot multistep reactions, avoiding need for interstep separation

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Chapter 3

Are Ionic Liquids Green Solvents?

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The examination of ionic liquids (ILs) as green solvents should include chemical and solvency characteristics, as well as environmental toxicological considerations. Ionic liquids can best be described as greener solvents, based upon current reactions and measured properties from the literature. Environmental impact and toxicity criteria can be used as measures to evaluate these compounds in terms of their environmental effects. These chemicals display a wide range of potential application as greener solvents.

Ionic Liquids as Greener Solvents

Ionic liquids are a new class of solvents, which offer alternatives to conventional molecular solvents in many chemical applications, with both the thermodynamics and kinetics of reactions carried out in ionic liquids being different from those in conventional molecular solvents. These solvents are often fluid at room temperature, and commonly consist of organic cationic species and inorganic anionic species; they have no measurable vapor pressure, and hence can emit no Volatile Organic Compounds (VOCs).

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

One indication of the growth in interest in these compounds is shown by the increase in the number of articles on this topic during a ten-year period. (Figure 1) The current year is only half over! The questions, observations and guidelines we offer here will assist in rating ILs as greener solvents. (1)

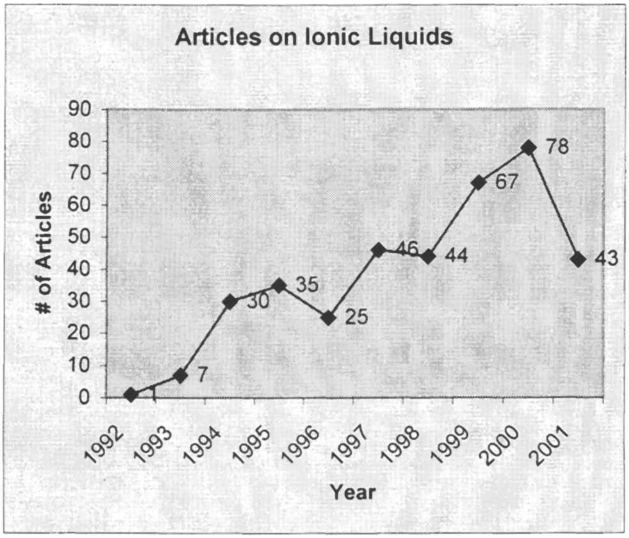

Figure 1. Increase in number of articles on ionic liquids over a ten-year period

Green perspectives

The principles of green chemistry provide a reference point for the chemical profession in trying to deal with the novel ethical considerations resulting from science and technology found in the 21st century.(2) The chemistry community must regard environmental protection as a *sine qua non*, offering opportunities to develop more cost effective processes and products.(3) This may be done in essentially two ways: Existing processes can be greened with existing technologies, or new technologies can emerge. Ionic liquids are a recent example of a hybrid of an existing technology (known solvents) that is maturing and being scientifically explored.

As ILs develop, it becomes essential to critically evaluate their chemistry and environmental impacts. A set of considerations are needed to help assess

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their "green-ness".(3) To begin developing these, let us first enumerate the drivers influencing green chemistry.(Table 1)

Table 1. Major drivers affecting green chemistry

Major Drivers
• Human Welfare
• Quality of Life
• Environmental Protection
• Sustainable Development

The challenge facing our world is to produce a sustainable civilization. This civilization should take from the earth only what is necessary for survival without compromising the potential of future generations. Chemistry has an important role to play in this effort.(4) In order to accomplish this three challenges must be met.(Table 2)

Table 2. Challenges to sustainable chemistry

Challenges
• Making renewable energy technologies a central component;
• Developing reagents that are obtained from renewable sources;
• Replacing polluting technologies by benign alternatives.

The obstacles to overcoming the challenges listed in Table 2 are shown in Table 3.

Table 3. Obstacles to overcoming challenges to a sustainable chemistry

Obstacles
• Incorporate environmental considerations into chemistry;
• Emphasize only chemistry that is really green;
• Avoid short-term and myopic thinking;
• Understand ethics of sustainability.

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What is a green solvent?

It will be difficult, if not impossible, to find a purely green solvent. Standards are needed for quantitatively and systematically evaluating solvents to allow chemists to clearly assess whether or not resulting chemistries and chemical processes are 'greener.' The first step regarding evaluating solvents is the development of traits and general criteria. The following table lists representative considerations.(Table 4)

Table 4. Traits and criteria for green solvents

General Traits and Criteria
• Generates less waste (in production, use, and disposal);
• Innocuous or more innocuous;
• Renewable resources in synthesis of solvents;
• Solve other environmental problems;
• Selectivity, reaction efficiency, efficient separation;
• Known hazards associated with solvents;
• Human & environment health effects are known.

It is not necessary for ionic liquids to possess all of these characteristics simultaneously to be considered *more green* (when compared to existing solvents). The results of this evaluation should indicate that effective use and reuse of ILs will contribute significantly to establishing them as a more environmentally benign solvent with reduced total impacts.(5) However, the traits and criteria should be used as a standard to rate the appropriateness of the use and/or development of these compounds in chemical applications.

Preliminary Evaluation of Ionic Liquids

An examination of the benefits of room temperature ionic liquids systems reveals they act as solvents for a wide range of chemical processes. Their most important advantage is probably that they have no measurable vapor pressure. This is a two-edged sword: no adventitious emissions, but introduction of potential challenges to recovery of products and solvent purification. When ILs serve as both catalyst and solvent, questions regarding changes the solvent is undergoing must be addressed. Increasing attention from industry, as they promise significant environmental benefits, will make answering those questions imperative.(6)

Even while chemical issues are being resolved, environmental/toxicological questions also need attention. The design of or the decision to use any solvent involves an analysis that utilizes the chemical structure to identify what part of a molecule is providing the characteristic or property that is desired from the products and what part of the molecule might be responsible for toxicity or hazard.(1) The goal or end result of this can be achieved through several different strategies, the choice of which is largely dependent on the amount of information that already exists. The information that will be useful is shown in Table 5. The lack of information regarding ILs in many areas illuminates needed areas of research before ionic liquids are clearly regarded as green solvents.

Table 5: Design and use of Green Solvents

Considerations for the Design and Use of Green Solvents
• Mechanism of action
• Structure-activity relationships
• Elimination of toxic functional group
• Reduce bioavailability
• Design for innocuous fate
• Minimization of energy consumption

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Greening of Ionic Liquids

Ionic liquids, being composed entirely of ions, were once mainly of interest to electrochemists. Recently, however, it has become apparent that, *inter alia*, a wide range of chemical reactions can be performed in them.(7)

As the interest in ionic liquids grows, there is a corresponding increase in the breadth of applications in which they are useful. It will be illuminative to briefly scan the current array of chemistries being conducted in this solvent system. This is not the complete list and the corresponding references have been selected.(Table 6) Interested readers are encouraged to search the literature.

The important point in this is that, as the ionic liquids are used more, the considerations in Tables 1-5 become more imperative.

Discussions and Future Directions

The present status of ionic liquids places them on the road to being a greener solvent. This is a healthy position not only for the segment of the chemical community which has a vested interest in them (researchers, suppliers and end-users) but for the chemical industry as a whole (as it provides an area that will be developed within green chemistry.) Let us now provide a preliminary evaluation of ILs as greener solvents.

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Table 6. Chemical applications of ionic liquids

Name organic reactions	
Diels-Alder reactions (19)	Weinreb amides
Friedel-Crafts (21)	Negishi cross-coupling
Heck reaction (22)	Claisen rearrangement
Trost-Tsuji C-C coupling	Stille coupling
Suzuki cross-coupling	Reformatsky Reactions

General Organic Reactions	
Proton donation	Hydroformylation (28)
Dimerization	Stereoselective syntheses
Hydrogenation	Ether cleavage and epoxide opening
Reductive carbonylation	
Polymer synthesis	Heterocyclic synthesis (29)
Hydroesterification	Benzoylation
Allylation (26)	Arylation (30)

Physical Organic Chemistry	
Electron transfer	Analytical chemistry
Organometallic synthesis (8)	Dipolar cyclo-additions

Inorganic Chemistry	
Oxide ion transfer	Supramolecular syntheses (31)
Synthesis of inorganic compounds	Electrochemistry (32), (33)

Catalysis	
Recycle catalysts	Homogeneous catalysis (34)
Immobilized catalysts (13)	Catalytic cracking (37)
Enzymatic catalysis (14)	Bioprocesses (35), (36)

Past and present

The early efforts (up until around 1992) with ionic liquids were based upon their desirable chemical properties. These properties were quite appealing in the area of electrochemistry, and afforded opportunities in basic and applied research. This has continued. The green aspects of these solvents may have been noticed, but certainly not emphasized. Up till this point the demand for environmental accountability was not fully appreciated.

The appearance of regulatory drivers in the early 1990's forced a reevaluation of the roles solvents play in chemistry and what constitutes desirable solvents. Some simple physical properties of the ionic liquids that make them interesting as potential solvents for synthesis are listed below.(12) These properties result in more "green" quality when compared to other solvents.(Table 7)

Table 7. Properties and benefits in ionic liquids

Physical Property		*Benefit*
• Good solvents for a wide range of both inorganic and organic materials	→	Unusual combinations of reagents can be brought into the same phase
• Often composed of poorly conducting ions	→	Highly polar yet non-coordinating solvents
• Immiscible with a number of organic solvents	→	Provide a nonaqueous, polar alternative
• Non volatile	→	Used in high vacuum systems

Even if one considers that the newer ionic liquids are free from many of the hydrolysis problems that make the halogenoaluminates(III) so difficult to handle, the breakdown products will include mineral acids (HX) and other acids from the breakdown of the anions (PF_6, BF_4, etc.). Even though most ammonium and imidazolium salts are hygroscopic and if used open vessels, hydration will almost certainly occur; these new ionic liquids are much easier to handle than the halogenoaluminate(III) systems.

Recent work has led to the development of a better physical understanding of ILs. (see Table 8) As good as these properties may seem to be, the evaluation of "green-ness" must continue, as valuable information is lacking. The information will come from several sources: expanded IL use and application in chemistry (even now an increasing range of reactions benefit from use of ionic liquids), measurement and systemization of physical properties, human and environmental toxicity tests (also taking advantage of molecular modeling) and the effects resulting from increased usage.

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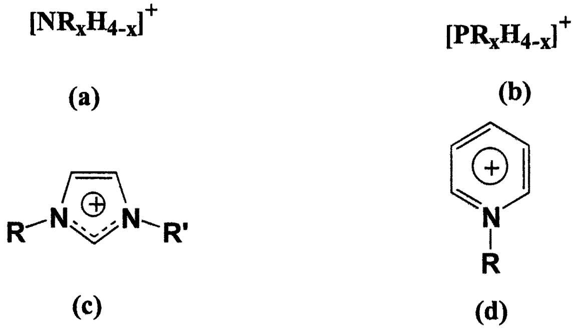
Table 8. Refined chemical properties of ionic liquids

Solvent Properties

- Polar phases (16)
- Solvent strength and polarity between acetonitrile and methanol
- Forms strong hydrogen bonds
- Shows conventional aromatic stacking
- Chloroaluminate ionic liquids can be both neutralized and buffered by the addition of an alkali halide (17)
- Liquid crystals are good solvents providing a partially ordered reaction environment

Evaluation: Preparation

Presently, the most common ILs in use are those with alkylammonium, alkylphosphonium, N-alkylpyridinium, and N,N'-dialkylimidazolium cations. (Figure 2)



$X = BF_4, PF_6, AlCl_4, NO_3, OTf$

Figure 2. (a) Alkylammonium, (b) alkylphosphonium, (c) N,N'-dialkylimidazolium, and (d) N-alkylpyridinium cations and common anions.

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Many alkylammonium halides are commercially available, or they can be prepared by the reaction of the appropriate halogenoalkane and amine. Preparation of the pyridinium and imidazolium halides may be similarly done. Other ionic liquids are made by the quarternerization of the appropriate amine. The synthesis procedures and source of raw materials should be scrutinized.

Examples of the typical methods for the preparation of ionic liquids contain areas that might be made more green. (Table 9, note: those shown are edited and should not be used in the lab!) The areas for improvement concern the use of elevated temperatures or pressures, use of halogenated reagents, excessive purification procedures and hazardous reagents. The goal is to make the IL progressively greener, from "cradle to grave."(25)

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Table 9. Example of preparation of ionic liquids (edited)

1-Butyl-3-methylimidazolium chloride, [bmim]Cl
1-methylimidazole (freshly distilled from CaH_2) and 1-chlorobutane and heated at 75 °C for 48 h under 3 bar pressure of dinitrogen. Excess chlorobutane was removed under reduced pressure with heating. The pale yellow molten product was crystallized on cooling as an off-white solid.
2.2.2 1-Butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF6]
[bmim]Cl in H_2O was cooled to 0 °C and hexafluorophosphoric acid was added. It was stirred for 2 h. The ionic liquid phase was washed with water, saturated aqueous $NaHCO_3$ solution and extracted into dichloromethane . The organic phase was dried over $MgSO_4$, filtered, the solvent removed and the ionic liquid dried for 6 h at 70 °C in vacuo.

Evaluation: Reaction chemistries

Two desirable characteristics of ionic liquids are apparent. First, they yield significant rate enhancement and high yield/selectivity. Second, they reduce two waste streams commonly associated with some traditional chemistries (through efficiency and catalysis).

1. The rate enhancement and high yield/selectivity must include improved and greener methods of isolation. Without this, the former is reduced. For example, a desirable discovery has been the ability to improve product isolation. This improved techniques results from extraction with supercritical carbon dioxide and it can further the 'greenness' of syntheses involving ILs.(20) Advances like these will be needed in the future.

2. Without a reliable and standard means for recycling the IL, it could become an undesireable wastestream. An example of this is provided by the Heck coupling of aryl halides or benzoic anhydride with alkenes, which can be performed with excellent yields in room-temperature ionic liquids. It has been shown that ILs provide a medium that dissolves the palladium catalyst and allow the product and byproducts to be easily separated. Consequently, the catalyst and ionic liquid can be recycled and reused.(11) This results in further increases in catalyst productivity.(23)

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Evaluation: Environmental considerations

It is necessary for usto think beyond the confines of the use of ionic liquids as merely a solvating medium. A recent review also claimed that 1-Alkyl-3-allcoxymethylimidazolium chlorides showed strong antimicrobial activity.(18) These must be substantiated, but they provide more evidence for the green-ness of ionic liquids. Most clearly, the lack of documented toxicity data is an area of necessary work. Anecdotal comments indicate safety in this regard, but the results from current work is critical. In the interim complete QSARS and modeling studies would help to assure favorable environmental profiles.

Three points must be highlighted:

1. Breakdown products and environmental lifetimes for ILs are needed;
2. Human and environmental toxicity studies will show ILs to be safe within use, but not benign;
3. Increased use will reveal unknown problems.

Conclusions: Report Card

Ionic liquids are becoming established as a potentially viable, environmentally benign alternative to existing solvents. They represent a greener alternative in many applications. As this maturation continues, green considerations for the evaluation of their development and use must also be continually raised.

Let us give an initial rating of the ILs.(Table 10)

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Table 10. Report card

Greening of Ionic Liquids	G	P	U
• Does the solvent use lead to less energy expenditure?		*	
• Does the solvated species react more efficaciously and selectively?	*		
• Does the solvent improve atom-economy?	*		
• What is solvent distribution into environment?			*
• Will the solvent be absorbed by organisms and how will it affect them?			*
• Is the solvent toxic? Can it be detoxified?			*

G: good; P: Poor; U: unknown

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Chapter 4

Organic Reactions in Ionic Liquids and on Supported Reagents

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Chemistry in ionic liquids and on metal oxides, taken mostly from the authors own work, will be described. It will be seen that ionic liquids compare favorably to metal oxide surfaces as reaction media and green phases.

Introduction

When the authors of this article started a very fruitful collaboration on organic reactions on metal oxide surfaces close to 25 years ago, the field was much like that of ionic liquids just a few years ago: there was very little activity. The area of surface organic chemistry has become very active in the last couple of decades and the area of ionic liquid chemistry, as attested by this symposium, is set to do the same.

We report below results from our laboratories on organic reactions in ionic liquids, the area of our second and more recent collaboration. Where similar

In Ionic Liquids; Rogers, R., et al.;
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results have been obtained on surfaces, a comparison of the chemistry in the two environments will be made. We also report our recent results of transition metal-chemistry on metal oxide surfaces where similar chemistry of others in ionic liquids has been published. It will be clear from this discussion that ionic liquids are already remarkably versatile and varied materials with great potential in synthetic, mechanistic, and green chemistry.

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Results and Discussion

Volatile Ionic Liquids

Nonvolatile ionic liquids (ILs) are of great current interest in part because, having little or no vapor pressure, they are potential replacements of volatile solvents. Nonetheless, volatile ILs are known and, in some instances, widely studied. Furthermore, results obtained on them can be extrapolated to the newer, less studied nonvolatile ILs. Without question the most familiar volatile IL is pyridinium chloride (m.p. 144°, b.p. 218°) which has been studied thoroughly by Royer. A synopsis of this and related work has been published [*1*].

The binary mixture of lithium perchlorate dissolved in diethyl ether (LP/DE), a medium that becomes an IL at LP=4.5 M because all the lithium ions are bound to ether [*2*], has been widely used in organic synthesis [*3*]. Interestingly, even in its IL form, LP/DE has significant vapor pressure [*4*]. Several theories have been offered on how this medium influences the rates and selectivities of organic reactions including a salt-induced change in polarity [*5*], normal catalysis by the Lewis acidic Li^+, and its internal pressure [*6*] which is large [*7*]. Internal pressure of the medium would influence the behavior of a reaction if it mimicked applied pressure which does influence rates of reactions. This is an important consideration because ILs are known or expected to have large internal pressures [*8*]. Furthermore, the internal pressure of a solute relative to that of a solvent affects the solubility of the solute in the solvent, an important consideration in some IL chemistry where biphasic behavior is important. Chemical, spectroscopic, and theoretical studies by us have clearly shown that the primary way in which LP/DE influences the behavior of reactions is by Li^+ catalysis [*9*]. Polarity and internal pressure play a much smaller role.

Although the chemistry of anions and neutral compounds supported on metal oxide surfaces is well known [*10*], the corresponding chemistry of supported cations is relatively unknown. Thus, a comparison of the catalysis of Li^+ in LP/DE and on a surface will not be made.

N,N-Dimethylammonium *N,N*-dimethylcarbamate ($Me_2NH_2^+Me_2COO^-$; Dimcarb), with a boiling point of 60° (with decomposition), is an inexpensive, widely used IL [11] and reagent in organic synthesis [12]. Recently, we have explored a few Diels-Alder (D-A) reactions, widely studied in other ILs [13], in this medium. Before presenting this work, a little background material on the D-A reaction is in order. The prototypical reaction of methyl acrylate (MA) with cyclopentadiene (CP) affords endo (N) and exo (X) adducts in an N:X ratio of about 3 that is not very sensitive to solvent polarity [14]. Much higher N:X ratios (15-20 to 1) are obtained when the reaction is catalyzed by Lewis acids. When MA is treated with CP on alumina, however, the ratio of adducts is very sensitive to the activity of the alumina used [15] in part because aluminum ions are exposed to the surface when alumina is activated by heating. On alumina activated at 300°, for example, N:X>50 has been obtained.

The results are far different in Dimcarb [16]. MA and also methyl vinyl ketone give only trace amounts of D-A products. Instead each dienophile undergoes conjugate addition with dimethylamine (Scheme 1). Acrolein, on the other hand, undergoes the D-A reaction exclusively with CP to yield N and X adducts in a 1.42 to 1 ratio (Scheme 2). When acrolein is treated with CP in the absence of solvent, a more endo-rich ratio of 3.68 to 1 ratio is obtained. Based on the work of MacMillan [17], a rational explanation can be given for the results in Dimcarb. $Me_2NH_2^+$ reacts with acrolein to give water and a new dienophile, an iminum ion, which reacts with CP to give N and X iminum ion products, hydrolysis of which by the water formed in the first step of the reaction yields $Me_2NH_2^+$ and the acrolein adducts but in a new ratio. $Me_2NH_2^+$ thus functions as a catalyst in Dimcarb. Exo selective D-A reaction would be very useful synthetically.

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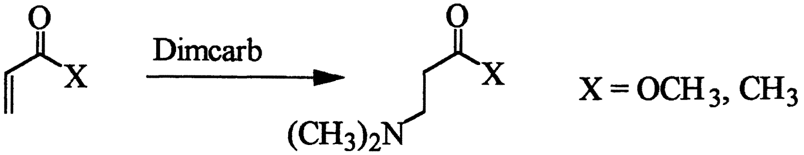
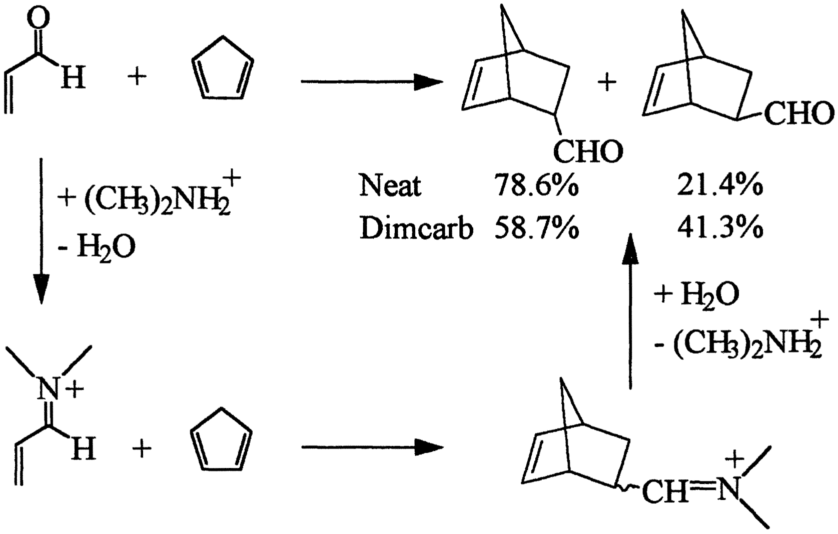


Scheme 1. Reaction of dienophiles with dimcarb.

Nonvolatile Ionic Liquids

1-Ethyl-3-methylimidazolium chloride (emimCl) /$AlCl_3$ and *N*-butylpyridinium chloride (BPC)/$AlCl_3$, which have little vapor pressure at room temperature, are remarkable ILs in part because they are liquid at or near room temperature over a wide range of salt to $AlCl_3$ ratios. In the acidic regime, where $AlCl_3$ is in excess, they and related media provide a good environment in which to generate carbocations via acid-base chemistry [18,19]. In acidic and basic regimes they provide suitable environments for cations and anions of all sorts



Scheme 2. Reaction of acrolein with cyclopentadiene.

generated in photoinduced electron transfer (PET) reactions. We will examine this fact by looking at the photochemistry of several anthracenes and stilbenes.

The photochemistry of anthracene (An) has been studied in solution for over 100 years [*20*]. More recently its photochemistry (and that of other polycyclic aromatic hydrocarbons [PAHs]) has been studied on the surfaces of solids as a model for its degradation in the environment by sunlight [*21*]. In most solvents including basic emimCl/$AlCl_3$ (emimCl in excess), the photochemistry yields a 4+4 dimer in the absence of O_2 (Table 1). The dimer is formed by reaction of the singlet excited state of An (An^{*1}) with An to form a complex which collapses to the product [*20*]. No ions are involved in this chemistry. In water, on the other hand, the reaction yielding two dimeric and two monomeric adducts is initiated by electron transfer from An^{*1} to the solvent [*22*]. In acidic emimCl/$AlCl_3$ ($AlCl_3$ in excess), the photochemistry is very unusual [*23*]. Even under very dry conditions there is always present a small amount of HCl, a superacid in the medium [*18,19*], and it protonates An at the 9 position to form AnH^+, a potential electron acceptor. The photochemistry is thus initiated by electron transfer from An^{*1} to AnH^+ to give $An^{+\bullet}$, a radical cation, and AnH•. Subsequent events are dictated by the fact that the IL is very poorly basic. In basic emimCl/$AlCl_3$, HCl is undoubtedly present but it doesn't protonate An and thus the photochemistry proceeds in a normal nonionic way. One can still find electron transfer chemistry in the basic IL, however, if O_2 is present [*24*]. Here anthraquinone (AQ) is the major product with lesser amounts of 9-chloro- and 9,10-dichloroanthracene being

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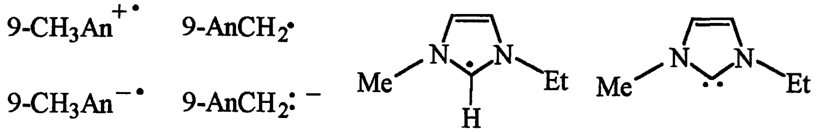
formed. The chlorinated products undoubtedly arise by reaction of $An^{+\bullet}$, formed by electron transfer from An^{*1} to O_2 to give $An^{+\bullet}$ and $O_2^{-\bullet}$, with Cl^-. The origin of AQ is not known but may involve singlet oxygen or $O_2^{-\bullet}$. Interestingly on aerated silica gel An affords the 4+4 dimer and AQ and several other products [*25*]; in deaerated silica, only the 4+4 dimer is formed [*25*].

Table I. Photochemistry of Anthracenes

Substrate	*Medium*	*4+4 Dimer*	*Electron Transfer*	*Electron Acceptor*
An	Basic EmimCl/$AlCl_3$	Yes	No	
An	Acidic EmimCl/$AlCl_3$	No	Yes	AnH^+
An	H_2O	No	Yes	H_2O
An	Basic EmimCl/$AlCl_3$ + O_2	No	Yes	O_2
An	Silica/O_2	Yes	Unclear	
9-MeAn	Basic EmimCl/$AlCl_3$	Yes	Yes	EMI^+
9-MeAn	Basic BPC/$AlCl_3$	Yes	Yes	BP^+
9-MeOAn	Basic EmimCl/$AlCl_3$	Unknown	Yes	EMI^+

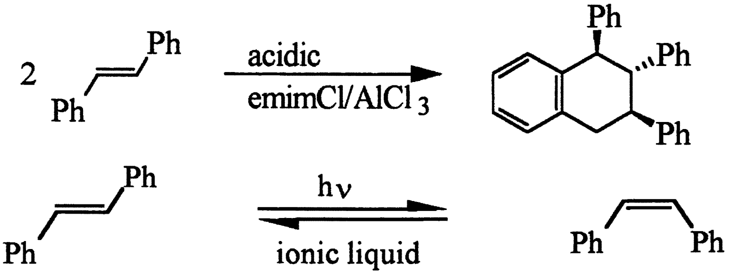
The photochemistry of the more easily oxidizable 9-methylanthracene (9-MeAn) in deoxygenated basic emimCl/$AlCl_3$ and basic BPC/$AlCl_3$ was described in 1996 [*26*]. Here a significant fraction of the photochemistry is initiated by electron transfer from $9\text{-}MeAn^{*1}$ to the aromatic cations, $emim^+$ and BP^+. As shown below, an array of ionic and neutral intermediates are formed in this photochemistry (Scheme 3). What distinguishes the photochemistry in the two ILs is not the initial electron transfer to the aromatic cations, both of which are exothermic and fast, but the fate of the reduction products, emim· and BP·. Emim·, with the greater reducing power, converts 9-MeAn into its radical anion, whereas the corresponding reaction with BP· is endothermic and doesn't occur.



Scheme 3. Transients formed in photochemistry of 9-MeAn.

The photoisomerization of *cis*- and *trans*-stilbene (c and t) has been studied extensively [*27*]. There are three established pathways by which the isomerization occurs: (1) the singlet mechanism in which direct irradiation affords singlet excited states, ^1t and ^1c, which cascade to a common twisted singlet state that in turn collapses with equal probability to ground state c and t; (2) the triplet mechanism in which the isomerization is initiated from triplet excited states, ^{3}t and ^{3}c, formed by triplet sensitization; and (3) the PET mechanism in which excited states of c and t transfer an electron to an acceptor to form radical cations from which the isomerization occurs.

In acidic emimCl/AlCl$_3$, t does not undergo a photochemical reaction, instead it yields *trans*, *trans*-1,2,3-triphenyl-1,2,3,4-tetrahydronaphthalene by an HCl-catalyzed dimerization (Scheme 4) [*28*]. As noted before, HCl in the acidic regime is acidic enough to protonated the substrate. In basic EmimCl/AlCl$_3$, t and c photoisomerize to give a photostationary state (PSS) consisting of about 56% t and 44% c [*28*]. In basic BPC/AlCl$_3$ the results are strikingly different; at the PSS there is more than 98% t.



Scheme 4. Chemistry of stilbenes in ionic liquid.

The photochemistry in BPC/AlCl$_3$ occurs by the PET mechanism. It is known from published work [*29*] that at the PSS there is little c if the PET is occurring. Calculations by us show that electron transfer from ^{1}t and ^{1}c to the easily reduced BP$^+$ is quite exothermic. Although the PET can also occur from triplet states, it isn't likely in the present case because electron transfer from ^{3}t and ^{3}c to BP$^+$ is endothermic in the first case and approximately thermoneutral in the second.

The photoisomerization in emimCl/AlCl$_3$ likely occurs by the singlet mechanism although the mole fraction of c and t at PSS is a little unusual. Even though the electron transfer from ^{1}t and ^{1}c may be exothermic, the amount of t and c at PSS is clearly not consistent with the PET mechanism. The amount of t and c at PSS generated by the singlet mechanism varies considerably, depending on the extinction coefficients (ϵ) of t and c at the wavelength used and the quantum yields (Φ) for t →c and c→t (Scheme 5). In most solvents, at 313 nm $(c)_{pss}$>90%, while at 254 nm $(c)_{pss}$~50%. In the present case where light>300 nm was used, a PSS rich in c is expected unless $\Phi_{t\to c}$ and $\Phi_{c\to t}$ are different in the IL.

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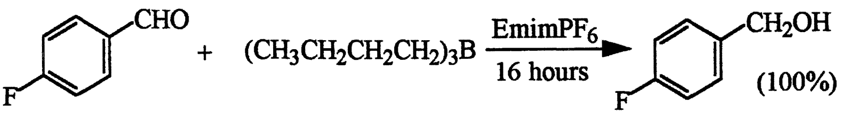
$$\left(\frac{t}{c}\right)_{ps} = \frac{\varepsilon_c \Phi_{c \rightarrow t}}{\varepsilon_t \Phi_{t \rightarrow c}}$$

Scheme 5. Ratio of t to s at photostationary state.

The rich photochemistry of t on silica/O_2 has recently been described [*30*], with c, phenanthrene, benzaldehyde and two 2+2 dimers being formed. The 2+2 dimers are perhaps of most interest because they are not formed in most solvents at low substrate concentration. They are formed on silica as a consequence of the fact that t forms ground state pairs on the surface [*30*]. In water where substrate aggregation is reasonable, t at very low concentration yields the same two 2+2 dimers [*31*].

The ILs of most current interest are those such as 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF_4) and 1-ethyl-3-methylimidazolium hexafluorophosphate (emimPF_6) which are made up of an heterocyclic aromatic cation and a nonbasic anion [*32*]. They are green phases because they have no vapor pressure, are nonflammable, and can be readily reused in most instances. They are currently being used in an array of organic and organometallic transformations [*32*].

One of us has recently reported the reduction of aliphatic and aromatic aldehydes with tributylborane in emimPF_6 and bmimBF_4 at 100° (Scheme 6) [*33*]. Previous attempts to use tributylborane as a reducing agent have required reaction temperatures of 150° or higher [*34*]. How the ILs abate the reaction temperature is unclear but the effect is dramatic.



Scheme 6. Reduction of aryl aldehyde in ionic liquid.

Trialkylboranes can also be converted into symmetrical ketones in EmimBF_4 using NaCN and trifluoroacetic anhydride [*35*]. For example, tributylborane is converted into 5-nonanone in 96% yield after a 24-hour reaction at 100° (Scheme 7). Unlike the reduction reaction above where 1 butyl group per borane is used, 2 alkyl groups are active here.

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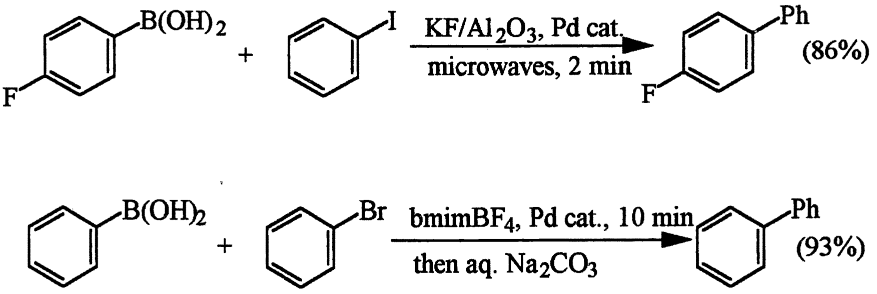
$$Bu_3B \quad + \quad \xrightarrow[EmimBF_4]{NaCN,\ (CF_3CO)_2O} \quad \xrightarrow[aq\ NaOH]{H_2O_2} \quad \underset{96\%}{(CH_3CH_2CH_2CH_2)_2CO}$$

Scheme 7. Synthesis of ketone in ionic liquid.

In spite of the vast literature on organic reactions on solids and supported reagents, there are only a few examples of reactions of organoboranes taking place on surfaces. We have, for example, studied the iodination [*36*] and bromination [*37*] of vinylboronic acids on alumina, with interesting results. More recently, we have examined in detail of the Suzuki reaction on very basic KF/Al_2O_3 [*38*]. As Welton and coworkers have carried out the Suzuki reaction in bmimBF_4 with good results [*39*], a comparison of the reaction in the solid and liquid green phases is interesting.

The Suzuki reaction is the Pd(0)-catalyzed coupling of an aryl- or vinylboronic acid with an aryl halide to form a biphenyl or styrene. The reaction requires a sacrificial base, KF/alumina which also serves as reaction medium in our case and aqueous Na_2CO_3 in Welton's (Scheme 8). The palladium usually consists of a Pd(0) complex such as $Pd(PPh_3)_4$ or a Pd(II) salt such as $Pd(OAc)_2$. Even in the latter case, it is generally assumed that the Pd(II) is reduced to Pd(0) before the coupling commences. Prior to our work, nobody had ever used palladium black as the catalyst in the reaction. Until the recent work of Buchwald [*40*] and Fu [*41*], which use unusual phosphine ligands, aryl chlorides were rather unreactive in the Suzuki coupling. The Buchwald and Fu reactions, of course, were run in volatile, flammable solvents. Aryl chlorides react sluggishly on KF/Al_2O_3 and in bmimBF_4. Representative examples of the Suzuki coupling in the two phases are shown below.



Scheme 8. Suzuki Reaction on KF/alumina and in ionic liquid.

A comparison of the Suzuki reaction on KF/Al_2O_3 and in bmimBF_4 is shown in Table II. Space limitations prevent a detailed discussion of this comparison.

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Suffice it to say that the reactions are remarkably alike, keeping in mind that our reaction is heterogeneous and Welton's is not, except when the aqueous Na_2CO_3, which is immiscible in $bmimBF_4$, is added. The Suzuki reaction works well in both phases. Where comparisons can also be made to reactions carried out in traditional solvents, the results in the two green phases stand up well. When comparisons can't be made, it is because the reactions on KF/Al_2O_3 and in $bmimBF_4$ have yet to be carried out.

Table II. A Comparison of the Suzuki Reaction in Two Green Phases

	Phase	
Characteristic	*KF/Al_2O_3*	*$BmimBF_4$*
vapor pressure	none	none
flammability	none	none
reaction conditions	in air, 80-100°, 3-4 hr	in air, 110°, 10 min
microwave activation	yes, for 2 min	unknown
recycle green phase	yes, with addition of KF	yes
palladium used	Pd black	$Pd(PPh_3)_4$
base	KF/Al_2O_3 itself	aq.Na_2CO_3
removal of product	by extraction	by extraction
reactivity of ArX	I>Br>Cl>F	I~Br>Cl
toleration of functional groups	yes	yes
kinetics	unknown	yes
yields	good to excellent	good to excellent

Conclusion

The volatile Dimcarb has been shown to give a more exo-selective Diels-Alder reaction. If this were generally true, the reaction would be synthetically useful. The two-component, non-volatile $emimCl/AlCl_3$ and $BPC/AlCl_3$ are good media for reactions involving cations and anions including the IL components themselves. Photoinduced electron transfer reactions occur commonly here. Acidic $emimCl/AlCl_3$ is superacidic and residual HCl protonates anthracene and catalyzes the dimerization of *trans*-stilbene. It is in fact possible to mimic the photochemistry of anthracene in acidic $emimCl/AlCl_3$ using CF_3SO_3H/CF_3COOH [*42*]. Basic $emimCl/AlCl_3$ and $BPC/AlCl_3$ are good media for photoinduced electron transfer, with $emim^+$, BP^+, and O_2 serving as electron acceptors. *cis-* and *trans*-Stilbene photoisomerize in both media. In BPC/$AlCl_3$ the isomerizations occur through stilbene radical cations. The one-component, non-volatile bmimPF_6 is useful in organoborane chemistry. The tributylborane induced reduction of aldehydes occurs at temperatures far lower than seen in other solvents. The Suzuki reaction occurring in two green phases, KF/Al_2O_3 and bmimPF_6, are remarkably alike.

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Experimental Section

Diels-Alder Reactions. The Diels-Alder reactions were run in the absence of solvent (neat) or in Dimcarb using a 1:1 molar ratio of cyclopentadiene and dienophile. When run in solution, 3 equivalents of Dimcarb were used. Reactions were run at room temperature for 12 hrs. Reactions mixtures were poured into water which were then extracted with CH_2Cl_2. Product mixtures were analyzed by gc/ms.

Photochemistry of *cis*- and *trans*-Stilbene.
(a) *Photolysis of trans-Stilbene in Acidic EmimCl/$AlCl_3$.* In a Vacuum Atmospheres glovebox, 200 mg of *trans*-stilbene was added to 13 g of freshly prepared emimCl/$AlCl_3$ (55% mol % $AlCl_3$). A bright yellow solution was immediately formed. Photolysis was carried out in a vacuum-sealed Pyrex glass tube in a Rayonet Type RS Photochemical Reactor using 3500 Å lamps. After 17 hours, the reaction mixture was quenched in ice water. The aqueous phase was then neutralized with 6M NaOH and the organic phase was extracted with methylene chloride. Product analysis was performed by GC-MS (HP 5890 gas chromatography and 5970 mass selective analyzer, with a crossbonded 100% dimethyl posiloxane column). The only product observed was the known *trans, trans*-1,2,3-triphenyl-1,2,3,4-tetrahydronaphthalene [*43*].

An identical sample was prepared and kept in the dark for 17 hours. Workup afforded only the above dimer.

(b) *Phtolysis of trans-Stilbene in Basic BPC/$AlCl_3$ (55 mol% BPC.*) Photolysis of *trans*-stilbene in basic BPC/$AlCl_3$ (154 mg in 12 g of melt) as described above for 17 hr afforded 96.7% *trans*-stilbene and 3.3% *cis*-stilbene. No other products were detected by gc/ms.

(c) *Photolysis of cis-Stilbene in Basic BPC/$AlCl_3$ (55 mol% BPC).* Photolysis of *cis*-stilbene (260 mg in 8.72 g of melt as described in part b above for 17 hr yielded 99.4% *trans*-stilbene and 0.6% *cis*-stilbene. There was also a trace of a compound with m/e = 142.

(d) *Photolysis of trans-Stilbene in Basic EmimCl/$AlCl_3$ (55 mol% emimCl).*

Photolysis of *trans*-stilbene (212 mg in 13 g of melt) as described above for 14.5 hr afforded 59.5% *trans*-stilbene, 27.1% *cis*-stilbene and trace amounts of unidentified products.

(e) *Photolysis of cis-Stilbene in Basic EmimCl/AlCl$_3$ (55 mol% emimCl).* Photolysis of *cis*-stilbene (260 mg in 7.2 of melt) as described above for 17 hr afforded 52.2% *trans*-stilbene, 41.1% *cis*-stilbene and lesser amounts of two unknown products with m/e = 142 (4.3%) and m/e = 180 (1.5%).

Preparation of 5-nonanone. Tributylborane (1 mmol), sodium cyanide (1.1 mmol) are added to a 10 mL round bottomed flask containing emimBF$_4$ (0.5 mL). The mixture is stirred at 100 °C for 24 hours. The mixture is cooled to RT and trifuoroacetic acid anhydride (1.2 mmol) is added and the mixture stirred for 1 hr. The intermediate is separated from the ionic liquid using ethyl ether (2 x 5 mL) and then oxidized using 30% H_2O_2 (3 mmol) and 3 N NaOH (1 mmol) to yield 5-nonanone (0.96 mole, 96%).

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Chapter 5

Ionic Liquids as Novel Diluents for Solvent Extraction of Metal Salts by Crown Ethers

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The efficiency and selectivity in solvent extraction of alkali metal salts, alkaline earth metal salts and lead salts from aqueous solutions into solutions of dicyclohexano-18-crown-6 (DC18C6) in 1-alkyl-3-methylimidazolium hexafluorophosphates, $[C_n\text{-mim}]PF_6$, have been determined. For competitive extractions of alkali metal salts and alkaline earth metal salts and single cation extractions of lead salts, the influence of systematically varying n in the room temperature ionic liquid from 4 to 9 and of anion variation in the metal salts is assessed.

Room temperature ionic liquids (RTILs) are receiving intense attention as solvents for a wide variety of organic reactions (*1-3*). Applications of RTILs in separations processes has received much less attention (*4-11*). In solvent extraction, the negligible vapor pressure and low flammability of RTILs are important advantages over conventional organic diluents. In metal ion separations, Dai and co-workers (*7*) observed large distribution coefficient values for extraction of strontium nitrate from aqueous solutions into solutions

In Ionic Liquids; Rogers, R., et al.;
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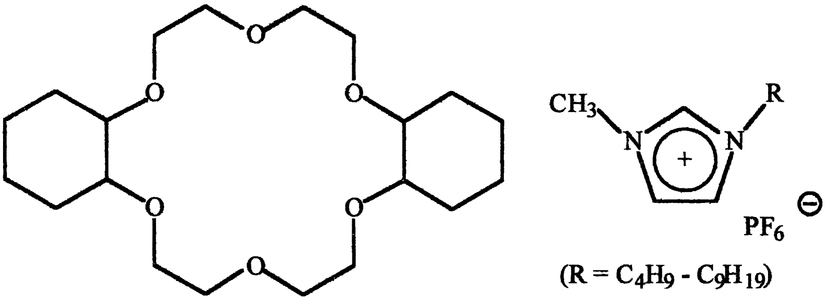

DC18C6

$[C_n\text{-mim}]PF_6$

Figure 1. Structures of dicyclohexano-18-crown-6 and 1-alkyl-3-methylimidazolium hexafluorophosphates.

of dicyclohexano-18-crown-6 (DC18C6) (Figure 1) in disubstituted imidazolium hexafluorophosphates and bis[(trifluoromethane)sulfonyl]amides. Subsequently, Rogers and co-workers (*9*) reported the extraction of sodium, cesium and strontium nitrates from aqueous solutions into 18-crown-6, DC18C6 and 4,4'(5')-di-(*tert*-butylcyclohexano)-18-crown-6 in 1-butyl, 1-hexyl- and 1-octyl-3-methylimidazolium hexafluorophosphates. Very recently, "task specific" RTILs containing metal ion chelating units and their use in the solvent extraction of Cd^{2+} and Hg^{2+} were described by Rogers and co-workers (*10*).

To probe the influence of systematic structural variation within RTILs upon metal salt extraction by DC18C6, we developed an improved preparation of 1-alkyl-3-methylimidazolium hexafluorophosphates, $[C_n\text{-mim}]PF_6$, with n = 4-9 (Figure 1). The influence of this structural variation within the RTIL and of the anion of the metal salts upon the efficiency and selectivity in competitive alkali metal salt and alkaline earth metal salt extractions by DC18C6 was determined. In addition, the single cation solvent extraction of lead salts by DC18C6 in the RTILs was investigated.

Improved Synthesis of 1-Alkyl-3-methylimidazolium Hexafluorophosphates

Although $[C_n\text{-mim}]PF_6$ RTILs have been utilized as solvents in many processes (*1-3*), no convenient method has been reported for the preparation of such solvents in large quantities and with sufficient purity for analytical studies.

We have developed a convenient, two-step procedure for the synthesis of $[C_n\text{-mim}]PF_6$ (Figure 2). In the first step, the neat reaction of 1-methylimidazole and equimolar 1-bromoalkane at 140 °C gave an essentially quantitative yield of the [C_n-mim]Br (*11*). An aqueous solution of the imidazolium bromide in a plastic bottle was stirred in an ice bath and one equivalent of 60 % aqueous hexafluorophosphoric acid was added slowly. After stirring in the ice bath and then at room temperature, the mixture was transferred to a separatory funnel containing water and one equivalent of triethylamine. The [C_n-mim]PF_6 was separated, washed with water, and dissolved in dichloromethane. The solution was washed with water and the dichloromethane was evaporated in vacuo. Traces of water were removed from the residue by azeotropic distillation with benzene using a Dean-Stark trap. The benzene was evaporated in vacuo and the resultant oil was dried at elevated temperature in vacuo. The overall yields of [C_n-mim]PF_6 with n = 4-9 were 64-87 % for the two-step process and increased as the 1-alkyl group was elongated (*12*).

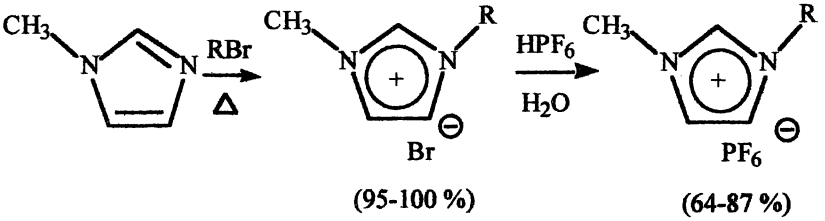

Figure 2. Synthesis of 1-alkyl-3-methylimidazolium hexafluorophosphates.

Solvent Extraction of Metal Salts by Dicyclohexano-18-crown-6 in 1-Alkyl-3-methylimidazolium Hexafluorophosphates

Competitive Alkali Metal Salt Extractions

To compare with solvent extraction results obtained for the RTILs, competitive solvent extractions of alkali metal chlorides by DC18C6 were performed in the frequently encountered diluents of chloroform, nitrobenzene and 1-octanol. From contact of 5.0 mL of 2.0 mM (in each) aqueous solution of the five alkali metal chlorides with 2.0 mL of 20 mM DC18C6 in the diluent, extraction of the alkali metal chlorides into the organic phase was undetectable (*12*). This low extraction efficiency is attributed to the high hydration energy of chloride ion (*13*).

Results from competitive solvent extractions of 2.5 mL of 2.0 mM (in each) aqueous solutions of the five alkali metal chlorides with 1.0 gram of 20 mM solutions of DC18C6 in [C_n-mim]PF_6 with n = 4-9 are presented in Figure 3. The level of extraction is given as the percentage of the crown ether that is complexed (loaded) by the metal ion. Since its loading did not reach 1 %, points

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for Li$^+$ are omitted from the graph. (The data are corrected for the levels of alkali metal cations that are extracted by the RTIL in the absence of DC18C6.) Immediately apparent is the very appreciable extraction of alkali metal cations by DC18C6 in the RTIL diluents under conditions that gave no measurable alkali metal cation extraction into chloroform, nitrobenzene or 1-octanol (*12*).

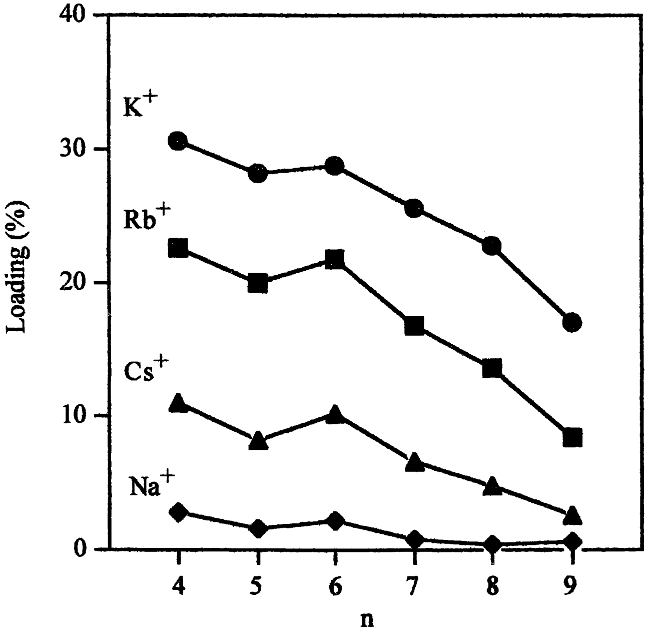

Figure 3. Influence of n variation in competitive alkali metal cation extraction from aqueous solutions by DC18C6 in [C_n-mim]PF_6.

With the exception of [C_6-mim]PF_6, there is a smooth decrease in the extraction efficiency for each alkali metal cation species as the 1-alkyl group is elongated. (Unusual behavior of [C_6-mim]$^+$ has been noted previously by others (*14*).) Thus, increasing the lipophilicity of the RTIL decreases the propensity for alkali metal cation extraction by DC18C6.

The observed extraction selectivity of K$^+$ > Rb$^+$ > Cs$^+$ > Na$^+$ > Li$^+$ is consistent with the relative complexing abilities of 18-crown-6 ligands for the alkali metal cations (*15*).

The influence of varying the 1-alkyl group of the RTIL diluent on the K$^+$/Cs$^+$ and K$^+$/Rb$^+$ selectivities for competitive alkali metal cation extractions

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by DC18C6 is shown in Figure 4. With the exception of [C_6-mim]PF_6, the K^+/Cs^+ selectivity and, to a lesser extent, the K^+/Rb^+ selectivity increase as the 1-alkyl group of the RTIL is elongated. Thus, the decrease in extraction efficiency as the 1-alkyl group of the RTIL is lengthened (Figure 3) is coupled with an increase in extraction selectivity (Figure 4).

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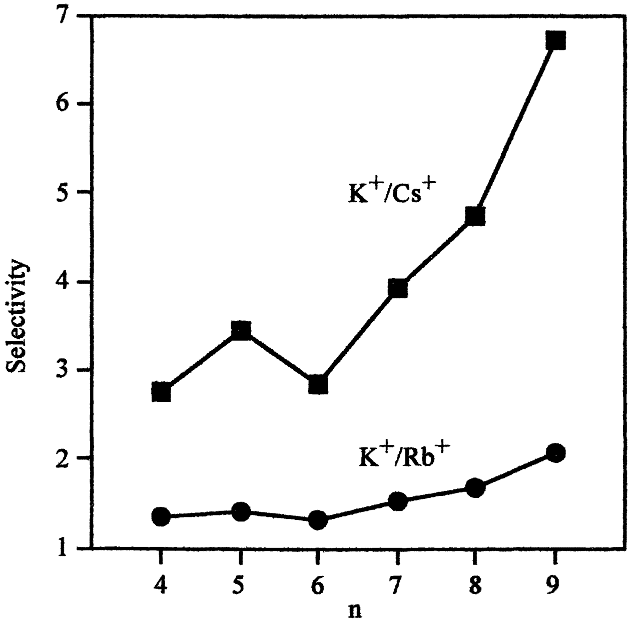

Figure 4. Influence of n variation upon K^+/Cs^+ and K^+/Rb^+ selectivities in competitive alkali metal cation extraction by DC18C6 in [C_n-mim]PF_6.

To evaluate the counterion influence in extractions involving RTIL diluents, competitive extractions of alkali metal chlorides, nitrates and sulfates from aqueous solutions by DC18C6 in [C_8-mim]PF_6 were performed. A comparison of the crown ether loadings for the five alkali metal cations as the anion was varied from chloride to nitrate to sulfate is presented in Table I. It is immediately apparent that the efficiencies and selectivities of alkali metal cation extraction are unaffected by variation of the aqueous phase anion. This differs markedly from results reported for competitive alkali metal salt extractions by DC18C6 in chloroform and 1-octanol (*16*, *17*). For these molecular solvents, the metal ion loading was strongly affected by anion variation. This further

Table I. Effect of Anion on Loading for Competitive Solvent Extractions of Alkali Metal Salts from Aqueous Solutions by DC18C6 in [C_8-mim]PF_6

	Loading (%)				
Anion	*Li^+*	*Na^+*	*K^+*	*Rb^+*	*Cs^+*
chloride	0.2	0.4	22.8	13.6	4.8
nitrate	0.2	0.4	22.3	13.2	4.6
sulfate	0.2	1.0	22.7	13.6	5.0

NOTE: Average from triplicate extractions with a standard deviation of ± 0.3 %.

underscores the unusual characteristics of RTILs as diluents in solvent extraction.

Competitive Alkaline Earth Metal Salt Extractions

For comparison with solvent extraction results obtained for the RTILs, competitive solvent extractions of four alkaline earth metal chlorides by DC18C6 were conducted in the molecular solvents of chloroform, nitrobenzene and 1-octanol. After contact of 5.0 mL of 2.0 mM (in each) aqueous solution of the four alkaline earth metal chlorides with 2.0 mL of 20 mM DC18C6 in the diluent, no extraction of alkaline earth metal cations into the organic phase was evident.

Results from competitive solvent extractions of 2.5 mL of 2.0 mM (in each) aqueous solutions of the four alkaline earth metal chlorides with 1.0 gram of 20 mM solutions of DC18C6 in [C_n-mim]PF_6 with n = 4-9 are presented in Figure 5. Since its loading did not reach 1 %, points for Mg^{2+} are omitted from the graph. As can be seen, very appreciable levels of Sr^{2+} and Ba^{2+} extraction are observed for the RTIL diluents; whereas there was no observable extraction of any alkaline earth metal cation with DC18C6 in the molecular solvents.

For Ba^{2+} and Sr^{2+}, there is a pronounced decrease in the extraction efficiency as the 1-alkyl group in the RTIL is elongated. Increasing the lipophilicity of the RTIL markedly diminishes the alkaline earth metal cation extraction efficiency. Sensitivity of the extraction efficiency for the alkaline earth metal cations (Figure 5) is much greater than that for alkali metal cations (Figure 3).

The observed extraction of $Ba^{2+} > Sr^{2+} >> Ca^{2+} > Mg^{2+}$ is in agreement with the relative complexing abilities of 18-crown-6 ligands for the alkaline earth metal cations (*15*).

The influence of varying the 1-alkyl group in the RTIL diluent on the Ba^{2+}/Sr^{2+} selectivity is shown in Figure 6. (With n > 7, the loading with Sr^{2+} was too low to accurately determine the selectivity ratio.) As was noted earlier for the alkali metal cation extractions, the loss in extraction efficiency with elongation of the 1-alkyl group (Figure 5) is coupled with increased selectivity (Figure 6).

In Table II is shown the effect of varying the anion of the metal salt in competitive extractions of alkaline earth metal chlorides, nitrates and perchlorates from aqueous solutions into DC18C6 solutions of [C_4-mim]PF_6. As

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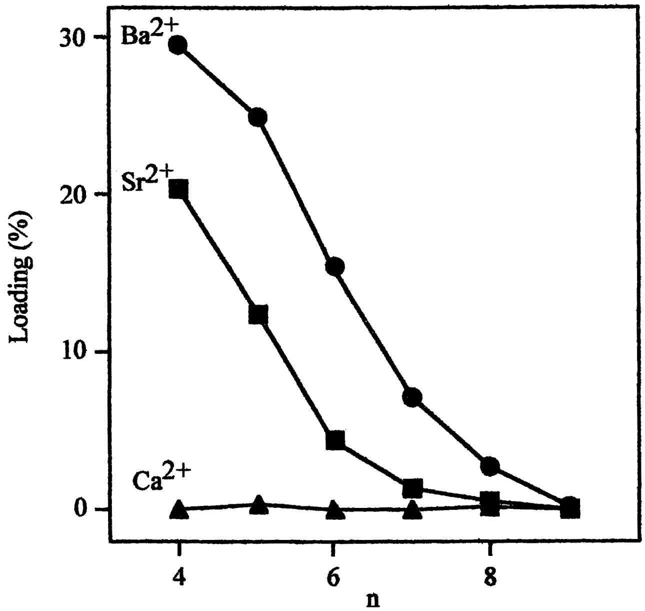

Figure 5. Influence of n variation in competitive alkaline earth metal cation extraction from aqueous solutions by DC18C6 in $[C_n\text{-mim}]PF_6$.

Table II. Effect of Anion on Loading for Competitive Solvent Extractions of Alkaline Earth Metal Salts from Aqueous Solutions by DC18C6 in $[C_4\text{-mim}]PF_6$

	Loading (%)			
Anion	*Mg^{2+}*	*Ca^{2+}*	*Sr^{2+}*	*Ba^{2+}*
chloride	0	0	20.3	29.6
nitrate	0.4	0.6	21.1	29.6
perchlorate	0.1	0.4	21.2	29.8

NOTE: Average from triplicate extractions with a standard deviation of ± 0.3 %.

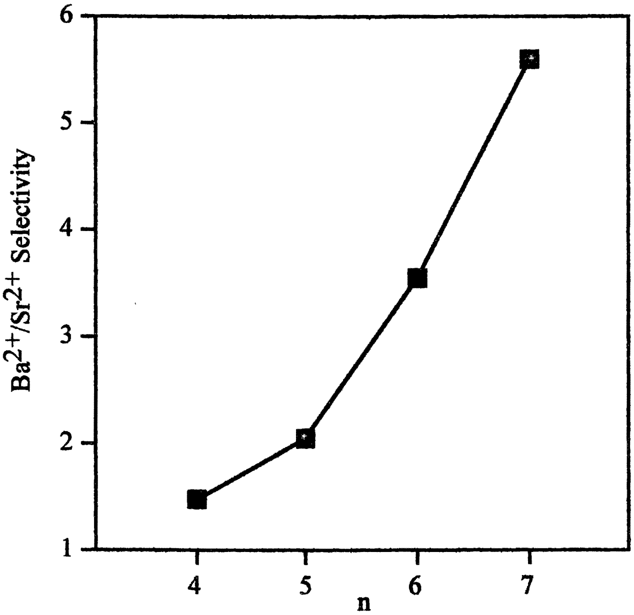

Figure 6. Influence of n variation on selectivity in solvent extraction of alkaline earth metal cations from aqueous solutions by DC18C6 in [C_n-mim]PF_6.

was observed for competitive extractions of alkali metal cations by DC18C6 in [C_8-mim]PF_6 (Table I), variation of the aqueous phase anion has no effect on the efficiency or selectivity of competitive alkaline earth metal ion extraction by DC18C6 in [C_4-mim]PF_6.

Lead Salt Extractions

DC18C6 has been utilized for complexation of Pb^{2+} in homogeneous media (*15*) and transport of lead salts across synthetic membranes (*18*).

For comparison with the solvent extractions results obtained for the RTILs, single metal salt extractions of lead nitrate by DC18C6 with molecular solvents of chloroform, nitrobenzene and 1-octanol were performed. From contact of 5.0 mL of 2.0 mM aqueous solutions of lead nitrate with 2.0 mL of 5.0 mM

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DC18C6 in the diluent, Pb^{2+} loading was 1.1 % with nitrobenzene and less with chloroform and 1-octanol.

Results from single cation solvent extractions of 2.5 mL of 2.0 mM aqueous solutions of lead chloride, nitrate and perchlorate with 1.0 gram of 5.0 mM solutions of DC18C6 in $[C_n\text{-mim}]PF_6$ with n = 4-8 are presented in Figure 7. (The data are corrected for the levels of lead salt extraction by the RTIL in the absence of DC18C6.) Since the formation of precipitates was noted for attempted extractions of lead chloride and lead nitrate by DC18C6 in $[C_9\text{-mim}]PF_6$, this RTIL was omitted from further investigation. Readily apparent in Figure 7 is the very appreciable level of Pb^{2+} extraction by DC18C6 in the RTILs under conditions that gave slight or no extraction by DC18C6 in chloroform, nitrobenzene or 1-octanol.

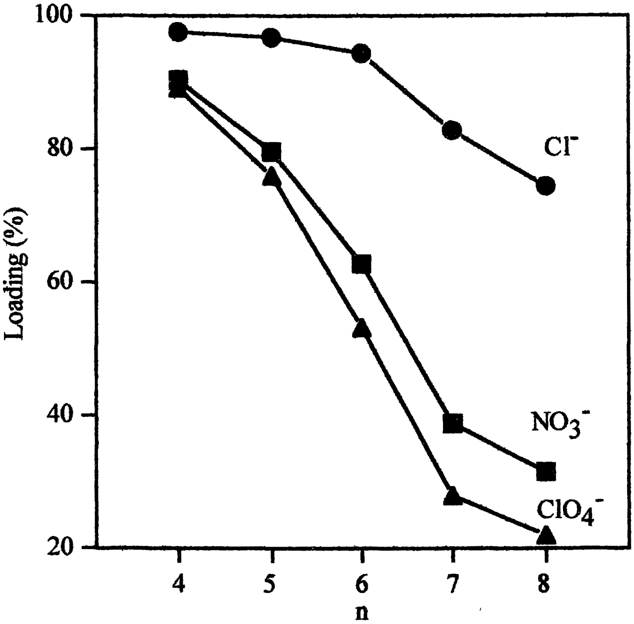

Figure 7. Influence of n and anion variation on efficiency of Pb^{2+} extraction from aqueous solutions by DC18C6 in $[C_n\text{-mim}]PF_6$.

As was the case for competitive solvent extractions of alkali metal cations (Figure 3) and alkaline earth metal cations (Figure 5) from aqueous solutions by

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DC18C6 in [C_n-mim]PF_6, the Pb^{2+} extraction efficiency decreases as n is increased and the RTIL becomes more lipophilic.

In contrast with the results presented earlier for alkali metal salt and alkaline earth metal salt extractions (Tables I and II, respectively), the identity of the lead salt anion is found to have a very significant affect on Pb^{2+} extraction efficiency. For lead chloride, the extraction efficiency is greater than with lead nitrate and lead perchlorate. This suggests that for lead chloride $PbCl^+$ is the species being extracted by DC18C6.

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Conclusions

Compared with molecular solvent diluents of chloroform, nitrobenzene and 1-octanol, solutions of DC18C6 in [C_n-mim]PF_6 provide markedly enhanced extractions of monovalent and divalent metal salts. For competitive extractions from aqueous solutions containing five alkali metal chlorides, the selectivity is $K^+ > Rb^+ > Cs^+ > Na^+ > Li^+$. The extraction efficiency decreases, but the selectivity is enhanced, when n in [C_n-mim]PF_6 is increased. For competitive extractions from aqueous solutions containing four alkaline earth metal chlorides, the selectivity is $Ba^{2+} > Sr^{2+} \gg Ca^{2+} > Mg^{2+}$. Again the extraction efficiency is observed to decrease, but the selectivity increases, when the 1-alkyl group in the RTIL is elongated. Solutions of DC18C6 in RTILs also effectively extract Pb^{2+}. In this case, the extraction efficiency is found to depend upon the anion of the lead salt with a higher level of lead chloride extraction than for lead nitrate and perchlorate. Further investigation of the applications of RTILs in separation processes is definitely warranted.

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Chapter 6

Supported Ionic Liquid Membranes and Facilitated Ionic Liquid Membranes

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Supported Liquid Membranes (SLMs) use porous supports impregnated with a solvent. In SLMs, solute molecules dissolve into the membrane at the feed/membrane interface. The dissolved species diffuse through the membrane and desorb at the opposite membrane surface. The addition of a third mobile chemical or carrier to the solvent that can reversibly bind to the dissolved species enhances the selectivity of the membrane (facilitated transport). Supported Ionic Liquid Membranes (SILMs) have an advantage over SLMs due to the negligible loss through vaporization of Room Temperature Ionic Liquids (RTILs) and the ability to selectively modify the properties of the membrane solvent. Our initial research focus was on the CO_2 separation from N_2 using RTILs with and

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without ionic and neutral doping compounds. Our chapter presents the proof-of-concept of SILMs, the basic principles of FILM development, and discusses future needs for continued development of SILMs and FILMs. Our SILM had a CO_2 permeability of 4.6 x 10^{-11} mol/(cm^2 kPa s) with a selectivity over air of 29; these values are competitive with existing membrane materials. The FILMs had a 1.8 improvement in CO_2 permeability with a driving force of 4.6 kPa of CO_2.

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Introduction - Membranes

Since this chapter reports on a project to combine membrane science with the chemistry of Room Temperature Ionic Liquids (RTILs), a review of membrane science is a logical starting point (*1*). A membrane is a semipermeable barrier that restricts the movement of molecules across it in a very specific manner. The following are some examples:

- Molecular Cut-Off Membranes for Bioseparations – The membranes have openings that hold back larger molecules while letting through smaller molecules. In this filtration process, molecular cut-off membranes separate large biomolecules from an aqueous solution.
- Reverse Osmosis Membranes for Desalination - This is a chemical solubility/diffusion process instead of a filtration process where water dissolves and transports through the membrane, which rejects the solutes and ions. The membrane material, therefore, preferentially dissolves and transports one chemical species over another.
- Contact Lenses – Allow the transport of oxygen.

Generically, eq. 1:

$$Q/A = j_i = L_i \Delta F \qquad (1)$$

defines the rate of transport through a membrane, where: $j_i = Q_i/A$ is the flux of the transport species, i; Q = quantity transported, A = surface area of the membrane, L_i is the membrane permeability or the inverse of the resistance to flux. The mode of transport through the membrane and the units of the driving force set the units of L_i. ΔF is the driving force or the difference in the potential of the transporting species across the membrane. In most membrane processes this potential is the chemical potential; however, other driving force potentials could be vapor partial pressure, electrical, magnetic, centrifugal, or gravity. Due to the thinness of membranes and, sometimes, the unknown thickness of the selective layer of the membrane, the distance over which the resistance to transport occurs may be included in L_i or the driving force term, ΔF.

Selectivity is a measure of the ability of a membrane to separate one chemical species, A, from a mixture of two chemicals, A and B. The ratio of the membrane permeability for A over the permeability for B is the membrane selectivity, defined as in eq. 2:

$$\text{Selectivity} = L_A/L_B. \qquad (2)$$

In a chemical solubility/diffusion membrane (examples are reverse osmosis or gas separation membranes), the ability to separate one chemical species from another depends on the membrane's ability to dissolve and diffuse one of the chemical species. In a gas-separation membrane, the gas dissolves in a polymer film and diffuses across the membrane. The difference in the solubility and diffusion coefficient of each species determines the selectivity of the membrane. In addition to polymers, researchers have also produced membranes from liquid solvents; thereby, opening a broader range of chemical solubility for exploitation in membrane separations.

Supported Liquid Membranes (SLMs) are porous solids that have their pores filled with the liquid. This arrangement (Figure 1) stabilizes the liquid. The flux through the membrane results from dissolution of the transporting species into the liquid followed by their diffusion across the membrane. One advantage of liquid membranes is the ability to add a mobile chemical species to the liquid that can reversibly bind to the transporting species. The mobile chemical species gives a second solution/diffusion transport pathway; "facilitated transport" is the name of this enhanced transport via a mobile chemical carrier additive. Since the mobile carrier enhances the solubility of only the chemicals with which it binds, facilitated transport also improves the selectivity of the membrane in addition to the flux.

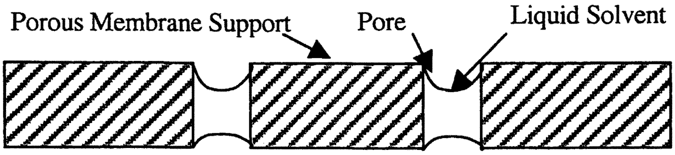

Figure 1. Illustration of a supported liquid membrane showing the liquid saturating the pores of a solid porous membrane support.

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The following are two limitations of supported liquid membranes:

- Loss of the liquid via volatilization or dissolution in contacting phases
- Loading limits (the solubility of the carrier in the liquid solvent)

This chapter proposes a new class of membranes that will diminish these two limitations along with opening up a new and broad range of chemical solubilities for exploitation in membrane separations. This new class of membranes will combine supported liquid membrane technology with the recent developments in room temperature ionic liquids. Acid gas separations (specifically carbon dioxide from air) will be the test case for the "proof-of-concept" of this new class of membranes.

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Introduction – Room Temperature Ionic Liquids

Room Temperature Ionic Liquids (RTILs) contain large, organic cations with a variety of anions that, together, melt near room temperature. In RTIL compositions, the 1-alkyl-3-methylimidazolium cation has been widely used to produce RTILs with useful properties for a variety of applications. Overall, RTIL properties are the result of contributions from both constituents; substituent groups on the cation fine-tune the physical properties (*2, 3*) and the anion is currently used to control the water miscibility.

RTILs based on PF_6^- or $N(SO_2CF_3)_2^-$ may find future applications as solvent replacements for traditional organic solvents in liquid/liquid separations (*2-4*). RTILs, in general, are good candidates for supported liquid membranes due to the following properties:

- RTILs dissolve complex materials, including many inorganic and organic compounds (*5, 6*)
- RTILs may be designed to be immiscible in organic solvents and water (*4*)
- RTILs may be non-volatile and can be used in vacuum systems
- Chemical modifications of both ions can be made to the ionic liquid for the production of specific application solvents or "designer solvents" (*7, 8*)
- RTILs modulate electrochemical complexation chemistry
- Addition of mobile carriers may enhance flux and selectivity (Facilitated Transport)
- RTILs may be non-flammable
- RTILs can have high thermal stability, up to 300 °C (*9*)

A key potential advantage of RTIL membranes over alternative supported liquid membranes is the ability to functionalize one of the ions to be a mobile carrier for facilitated transport. Such functionalization should have the following advantages that address the limitations of alternative supported liquid membranes:

- High carrier loadings (up to a mole fraction of 1)
- Anchoring the carrier inside of the membrane liquid
- Higher stability and flux rates than existing liquid membranes
- Enhanced selectivity of the liquid membrane

Unlike traditional organic solvents, RTIL properties may be adjusted by structural modification of the cation or anion to produce a solvent for a specific application. The potential exists for the incorporation of complexing agents into one of the ions resulting in a mole fraction loading much greater than the loadings that can be obtained when the complexing agent is an additive. For example, Davis (*8*) has produced RTIL cations containing an amine group for acid gas removal. In ordinary amine extractions systems, the amine loading in the solvent is only 0.1 mole-fraction; 1/10 of the theoretical loading capacity of the RTILs reported by Davis (*8, 10*).

Stabilizing a Liquid in a Porous Membrane

This section discusses the establishment and maintenance of RTIL impregnated pores as depicted in Figure 1. The establishment of the stabilized liquid within the pores of the membrane is a process of saturating a porous membrane with the RTIL. Two factors affect this saturation process: first, the wettability of the solid membrane material with the RTIL; and, second, the representative pore size of the membrane. The smaller the pore size of the membrane, the greater is the stability of the liquid membrane due to capillary forces.

Once the pores contain the liquid, the operational conditions of the membrane process must ensure the maintenance of the liquid within the pores. If the cross-membrane pressure exceeds the capillary forces of the liquid/solid membrane interface, the interface will retreat into the membrane and open up a pathway across the membrane; thereby, destroying the barrier aspect of the membrane. The maximum cross membrane pressure, being a function of capillary forces, is dependent on pore size, contact angle, and the surface tension of the stabilized liquid. Here RTILs have an advantage over alternative solvents since the surface tensions of RTILs (approximately 50 dynes/cm, (*11*)) are a factor of 2 or more above other organic solvents.

The RTIL used for this study was 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]). The choice of this RTIL resulted from the existence in the literature of physical data, such as viscosity and density, for [bmim][PF_6] that is not generally available for other RTILs.

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We qualitatively determined the wettability of [bmim][PF_6] on representative material surfaces. The order of decreasing [bmim][PF_6] wettability of the surfaces was polycarbonate > stainless steel (304) and aluminum (6061T5) > Teflon. The solid supports for supporting ionic-liquid membranes need to be 'ionic liquid-philic'; meaning that the contact angle of the ionic liquid on the solid surface must be less than 90° (measured through the ionic liquid) in order for capillary forces to stabilize the liquid in the membrane pores. During the qualitative testing, the surfaces that were ionic liquid-philic were also hydrophilic surfaces. This order indicates that [bmim][PF_6] wets hydrophilic surfaces, and therefore, the solid membrane support material should be hydrophilic.

We then proceeded to saturate two hydrophilic porous polymer membranes with [bmim][PF_6] by first contacting the polymer membrane with the ionic liquid, allowing it to soakup the liquid. Both porous membranes initially became translucent after soaking up the [bmim][PF_6]. The two hydrophilic porous polymer membranes saturated with [bmim][PF_6] were:

- Millipore GVWP: 0.22 μm pore size, hydrophilic Polyvinylidene Fluoride (PVDF) , 125 μm thick
- Gelman Sciences Supor 200: 0.2 μm pore size, hydrophilic Polyethersulfone (PES), 152 μm thick

The following are observations of the saturated polymer membrane supports:

- The Millipore PVDF warped and became cloudy with time
- The Gelman Sciences PES showed no physical change with time (remained translucent) and showed no signs of warping or swelling

Therefore, the hydrophilic polyethersulfone (PES) appears to provide a stable, saturated support for [bmim][PF_6] without polymer swelling and is the polymer support used for the stabilized room temperature ionic liquid membranes (RTIL membranes or SILMs) reported in the remainder of this chapter. We have tested this PES stabilized RTIL membrane to cross-membrane pressures of 20 kPa. However, we estimate that these membranes can support cross membranes pressures of 480 kPa based on a membrane pore size of 0.1 μm and an RTIL surface tension of 50 dynes/cm.

Experimental Procedures and Materials

Membrane Formation

The RTIL used in this study was [bmim][PF_6] synthesized as in reference *11*. The SILM formation process was the contacting of the Gelman Sciences Supor

200 membrane (0.2 μm pore size, hydrophilic Polyethersulfone (PES), 152 μm thick) with the RTIL, allowing it to soakup the liquid. The PES membrane remained submerged in the RTIL for a period of one hour to overnight. Finally, the excess RTIL was wiped from the surface of the membrane with unsaturated PES prior to the membrane installation into the Batch Membrane-Flux Test Unit (described below). The doped or facilitated transport membrane formation followed the same procedures except that dopent was dissolved into the $[bmim][PF_6]$ prior the PES membranes soaking up the RTIL solution.

Apparatus and Analytical Equipment

Gas Sorption Test Unit

The gas sorption test unit was an in-house produced unit for determination of the sorption isotherms of gases by liquids or solids. It consisted of two parts. The first part was a thermal control chamber for holding the test equipment at a constant temperature. The second part was a dual-chamber hand-blown glassware for holding the sorbent and the gases to be sorbed, Figure 2.

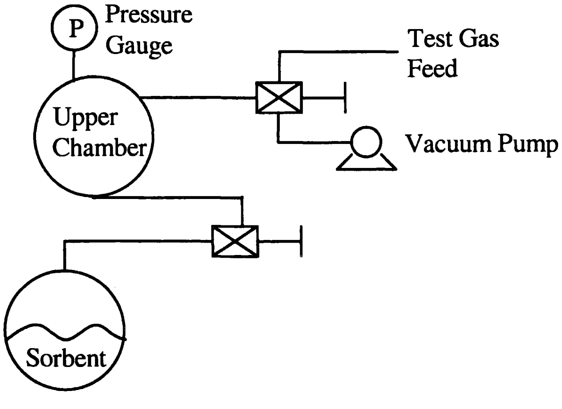

Figure 2. The Gas Sorption Test Unit showing the upper chamber for receiving an initial charge of test gas before contacting the sorbent in the lower, removable chamber.

The thermal control chamber was an insulated box 0.50 m wide x 0.76 m high x 0.45 m deep. Within this box, a heat source (light bulb) connected to a temperature controller provided variable temperature control. The dual chamber

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glassware, Figure 2, had an upper chamber (16.8 mL) for isolating the initial gas charge before contacting the sorbing material in the lower chamber (13.5 mL). The upper chamber also had a pressure gauge for monitoring the gas sorption during the experiment. The lower chamber was removable and held the sorbent material.

Batch Membrane-Flux Test Unit

In the batch membrane-flux test unit (Figure 3), the membrane was a barrier between two sealed chambers containing equilibrated volumes of air or nitrogen (i.e., at the same pressure). The volume of the upper or "feed gas" chamber was 80.4 mL and the volume of the lower or "permeate" chamber was 94.6 mL. A known quantity of the solute gas was injected into the "feed gas" chamber. This injection produced a partial pressure difference in the solute gas across the membrane. Measurement of the solute gas flux across the membrane came indirectly from measuring the total pressure increase with time in the lower or "permeate" chamber. The two sealed chambers were stainless steel.

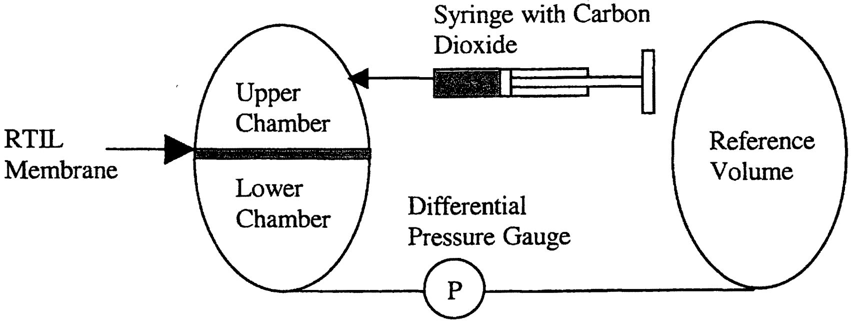

Figure 3. The Batch Membrane-Flux Test Unit showing the upper or "feed gas" chamber receiving an initial charge of carbon dioxide with the flux into the lower or "permeate" chamber being monitored by a pressure gauge.

Methods and Procedures

Sorption of Atmospheric Gasses by [bmim][PF_6]

Based on the discussion in the Introduction, the ability of a liquid membrane to separate carbon dioxide from air depends in part on the preferential sorption of the liquid membrane for carbon dioxide over the other chemical components of

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air. For this reason, the starting point for evaluating RTIL membranes for carbon dioxide gas separation was the determination of the [bmim][PF_6] Henry's Law Constants for carbon dioxide, oxygen, and nitrogen using the previously described gas sorption test unit. The procedure was to place a known volume of [bmim][PF_6] into the test unit's lower chamber and then draw a vacuum to degas the sample. *Safety Note: Degas for less than 5 minutes. Prolonged vacuum treatment of water containing [bmim][PF_6] may promote the breakdown of the anion, [PF_6]$^-$, into hydrogen fluoride and PF_5 gas via a shift in the following equilibria:*

$$H_2O_{(l)} \Leftrightarrow H^+ + OH^- \qquad (3)$$

$$H^+ + PF_6^- \Leftrightarrow HPF_6 \Leftrightarrow HF + PF_{5(g)} \qquad (4)$$

Next, with the lower and upper chambers isolated, the test unit's upper chamber received known moles of the test gas (carbon dioxide, oxygen, or nitrogen). The upper and lower chambers were then connected and the gas/[bmim][PF_6] system allowed to equilibrate. Figure 4 plots the vapor pressure and gas uptake of the liquid at equilibrium. Finally, without degassing, the process was repeated and the new vapor pressure and cumulative gas uptake of the liquid were plotted in Figure 4. The slope of the cumulative uptake vs. equilibrated vapor pressure is the Henry's Law Constant for the test gas in the RTIL.

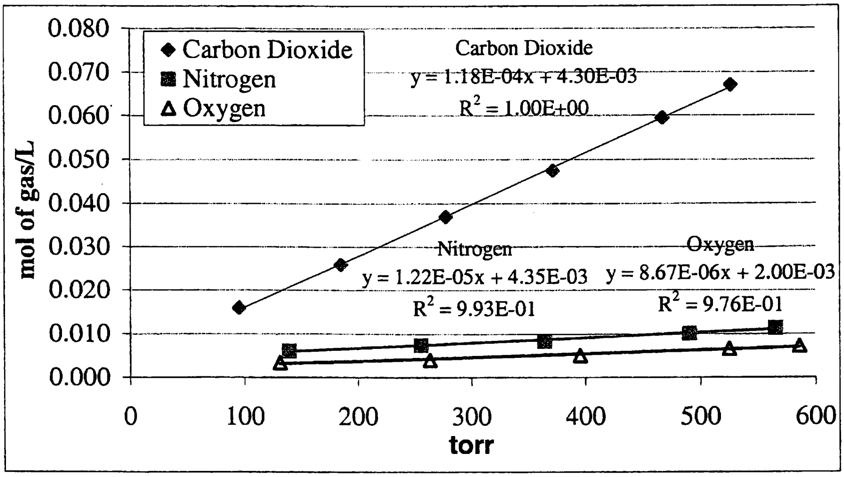

Figure 4. [bmim][PF_6] gas sorption isotherms for carbon dioxide, nitrogen, and oxygen (sorption at 27.5 °C). Note that the slopes are the Henry's Law Constants. The y-intercepts are experimental artifacts.

Gas Flux Experiments

Figure 3 is a sketch of the equipment for measuring gas flux through the stabilized ionic liquid membranes. The measurement of gas flux started with charging the upper and lower chambers in Figure 3 with the same pressure of air or nitrogen. Next a known volume of the carbon dioxide (2 to 20 mL) was injected into the upper chamber. The raw data was the change in pressure of the lower chamber with time. This change in pressure was due to the flux of carbon dioxide since the partial pressures of air (or nitrogen) on both sides of the membrane were equal. The initial slope of the raw data over 60 min, after a lag time of 0 to 20 min, was the flux rate under the test conditions.

To measure the flux rate of air, for the determination of membrane selectivity, the procedure was the same except that a known volume of air was injected, not carbon dioxide. Also due to the low air flux, the initial slope data was taken over 1400 min.

The "humid" flux conditions were produced by injecting 0.2 mL of liquid water into the upper chamber of the test unit and allowing both chambers to come to vapor equilibrium with the liquid water before injecting the carbon dioxide. The injected liquid water did not contact the membrane. The "non-humid" flux conditions used membranes in equilibrium with room air. These test conditions affect the [bmim][PF_6] water content since the water content of [bmim][PF_6] is 11700 ppm (equilibrated with water) or 590 ppm (after a drying procedure) (*11*).

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Gas Sorption Isotherms

Figure 4 shows the gas sorption isotherms of [bmim][PF_6] for the three atmospheric gasses of interest to this study, carbon dioxide, nitrogen, and oxygen. The slope of the isotherm gives the relationship between the solubility of the gas and its vapor phase partial pressure and is the [bmim][PF_6]'s Henry Law Constant for the gas. For comparison, the carbon dioxide isotherm's slope is 2.6 times the Henry's Law Constant for carbon dioxide in water (totaled for all aqueous carbon dioxide species, $CO_{2(aq)}$, bicarbonate, and carbonate). Figure 4 shows a 10-fold preference of [bmim][PF_6] for carbon dioxide over the main atmospheric gasses of nitrogen and oxygen. This preference is shown in the slope of the respective isotherms. This preference in solubility indicates that a [bmim][PF_6] liquid membrane potentially could separate carbon dioxide from air. Note that the isotherms in Figure 4 are for [bmim][PF_6] not in equilibrium with water; in the terminology used later in this chapter, the isotherms are for "non-humid" not "humid" conditions.

CO_2/Air Separation

Figure 5 shows the results of carbon dioxide flux through the [bmim][PF_6] membrane for a range of cross membrane differences in carbon dioxide partial pressures. For comparison with alternative stabilized liquid membranes, Figure 5 also shows data from a Starburst Polyamidoamine (dendrimer) stabilized liquid membrane (*12*). The membrane permeability for carbon dioxide, L_{CO2} in eq. 1, is the slope of a linear fit line to the data in Figure 5. The [bmim][PF_6] membrane carbon dioxide permeability in Figure 5 is 4.62 x 10^{-11} mol/cm^2 kPa sec. Our measured permeability of air through a [bmim][PF_6] membrane (data not shown) is $\leq$ 1.58 x 10^{-12}. Based on eq. 2, the [bmim][PF_6] membrane selectivity for carbon dioxide over air is $\geq$ 29. Reported polymer membranes have selectivities for CO_2/air around 15 to 35; the reported selectivity of the dendrimer membrane at a 40 kPa carbon dioxide driving force was 700 (*12*).

The differences in Henry's Law Constants from Figure 4 would predict a [bmim][PF_6] membrane CO_2/air selectivity of 10 not $\geq$ 29. The greater measured selectivity over that predicted could come from an additional diffusion selectivity of the dissolved species in the [bmim][PF_6]. Another consideration is that the [bmim][PF_6] membrane was in equilibrium with room air and, therefore, may have had a higher water content than the [bmim][PF_6] liquid reported in Figure 4. Water content in [bmim][PF_6] may increase the solubility of carbon dioxide vs. nitrogen or oxygen. Later sections in this chapter further discuss the effect of [bmim][PF_6] water content on carbon dioxide flux.

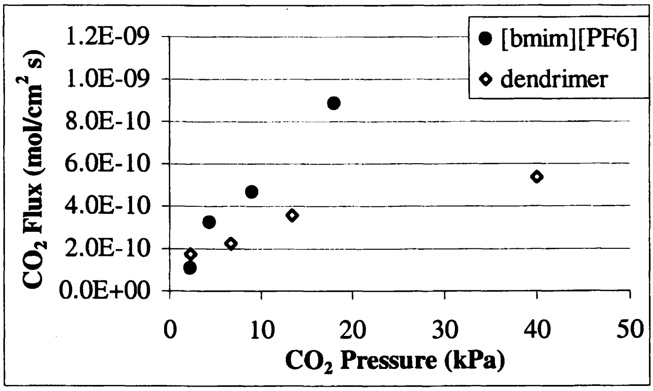

Figure 5. Flux vs. CO_2 driving force for [bmim][PF_6] and Starburst Polyamidoamine (dendrimer) stabilized liquid membranes. The data shows that RTIL membrane permeabilities are competitive with existing membrane materials.

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CO_2-Facilitated Transport

The previous sections provide the "proof-of-concept" for formation of a stabilized RTIL membrane for acid gas separations. The results are favorable when compared to existing stabilized liquid membranes. The following sections evaluate the potential for facilitated transport in RTIL membranes. The concept of facilitated transport for carbon dioxide, as discussed in the Introduction, would involve the addition of a mobile chemical species, or carrier, to the RTIL that can reversibly bind to CO_2. This would enhance the solubility of only CO_2 increasing the selectivity of CO_2 over air during membrane transport. The mobile chemical carrier would supply an additional solution/diffusion transport pathway, which is facilitated transport. We considered the following three types of carriers:

- Neutral Amines
- Functionalized RTILs
- Ammonium Salts

In this chapter, we consider only amine chemistry for the carriers. Tertiary amines require water to react with carbon dioxide (*10*) (eq. 5):

$$CO_2 + NR_3 + H_2O \Leftrightarrow NR_3H^+ + HCO_3^- \qquad (5)$$

and, as such, a tertiary amine carrier will only work with RTILs that absorb water, like [bmim][PF_6]. The CO_2-binding equation for primary and secondary amines is shown in eq. 6:

$$CO_2 + 2R_2NH \Leftrightarrow R_2NH_2^+ + R_2NCOO^- \qquad (6)$$

The secondary amine, diethanolamine (DEA), has literature references for its use as a carrier in supported liquid membranes; however, Yamaguchi, *et al.* (*13*) found that the primary amine, ethylenediamine (EDA), had a large facilitating effect in an ion-exchange membrane (Nafion 117). In ion-exchange membranes with amine concentrations of approximately 0.4 M, Yamaguchi, *et al.* observed that the primary amine had twice the facilitating effect as the secondary amine. The amines from the Yamaguchi, *et al.* study are the logical starting point for facilitated transport in RTIL membranes since both systems are highly ionic environments with carbon dioxide solubilities in the same order of magnitude, water vs. [bmim][PF_6].

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Neutral Amine Carriers

Table I lists the neutral amines examined in this study, the observations of the solubility of the carrier, and the solubility of the carrier after exposure to carbon dioxide (the formed carbamate). In order for the facilitated transport to occur, both the bound and unbound carrier must be soluble in the liquid membrane. The data in Table I comes from visible observations; for instance, the EDA/[bmim][PF_6] mixture stabilized membrane after exposure to carbon dioxide developed large areas of brown precipitate on the feed side of the membrane. In addition the EDA/[bmim][PF_6] mixture, not stabilized in the polymer membrane, became cloudy and more viscous after exposure to room air. The DMP/[bmim][PF_6] mixture (where DMP = 1,2-diamino-2-methylpropane), not stabilized in the polymer membrane, also formed sediments after exposure to room air; however, no visible change occurred to the stabilized membrane after exposure to carbon dioxide.

Figure 6 shows the carbon dioxide flux vs. cross membrane differences in carbon dioxide partial pressures for [bmim][PF_6] membranes doped with the neutral amine carriers in Table I that were soluble in [bmim][PF_6] in both the carbon dioxide bound and unbound forms. The longest line in Figure 6 is the linear fit for the undoped, non-humid [bmim][PF_6] membrane or the "baseline" case. The added neutral amine carriers did not result in any improvement in carbon dioxide flux through the [bmim][PF_6] membranes. In fact, the MCHA/[bmim][PF_6] membrane exhibited decreased flux when compared to the baseline case.

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Table I. Miscibility of Potential Neutral Carriers[a] and Their Carbamates

	Soluble in [bmim][PF_6]?	*Carbamate Soluble?*
Primary Amines		
Ethylenediamine (EDA)	Yes	No
1,2-Diamino-2-methylpropane (DMP)	Yes	No (?)
Cyclohexylamine (CHA)	Yes	Yes
Secondary Amines		
Diethanolamine (DEA)	No	---
N-Ethyl-Cyclohexylamine (ECHA)	No	---
N-Methy-Cyclohexylamine (MCHA)	Yes	Yes
Tertiary Amines		
N,N,N',N'-Tetramethylethylenediamine (TMEDA)	Yes	Yes

[a] Mole Fractions = 12% to 20%, except EDA = 36%

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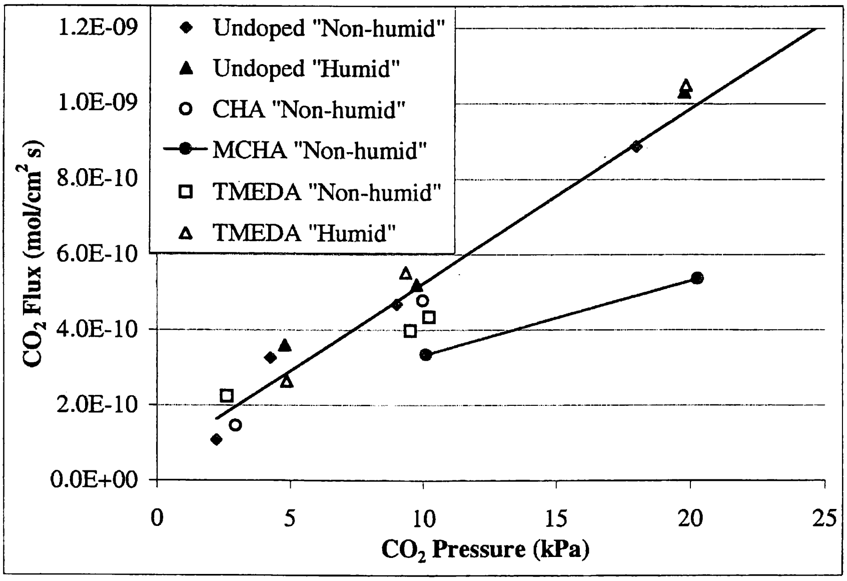

Figure 6. Neutral amine-facilitated CO_2 flux from air or nitrogen for [bmim][PF_6] membranes. The carrier concentrations in [bmim][PF_6] were 0.2 mole fraction. "Non-humid" flux conditions used membranes in equilibrium with room air; while, "humid" flux conditions used membranes in equilibrium with water saturated air.

Ionic Carriers

That the primary amines EDA and DMP (Table I) came out of solution in [bmim][PF_6] when exposed to carbon dioxide may be understood as the carbamates of the diamines forming salt crystals. In light of this and the data in Table I, the best option might be an ionic amine. An ionic carrier could anchor the carbamate in solution.

Two approaches seem plausible to obtain ionic amines. The first is to incorporate an amine group into one of the nitrogen substituents of a disubstituted imidazolium ion; such as, replacing the butyl group in [bmim][PF_6] with an amine containing group (Figure 7). We have tested (not reported here) tertiary amine-functionalized room temperature ionic liquid membranes. Alternatively, an organic salt with an amine function could be added to [bmim][PF_6]. While the organic salt may not be a liquid at room temperature, the salt/[bmim][PF_6] solution could be.

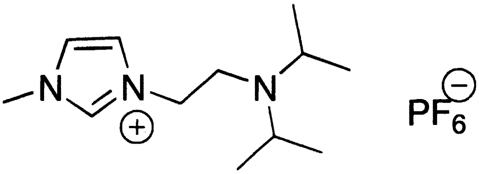

Figure 7. An example of a functionalized room temperature ionic liquid for facilitated transport of carbon dioxide. The functionalization shown is a tertiary amine.

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We tested a primary, secondary diaminophosphonium bromide salt (DiAPS), $[\phi_3P^+(\text{-}CH_2\text{-})_2NH(\text{-}CH_2\text{-})_2NH_2][Br^-]$, as a facilitated transport carrier for carbon dioxide. At a concentration of 0.15 mole fraction, both the salt and its carbamate were soluble in [bmim][PF_6]. Figure 8 shows the carbon dioxide flux through the DiAPS/[bmim][PF_6] membrane for a range of cross-membrane differences in carbon dioxide partial pressures. For comparison, Figure 8 also shows data for the baseline, undoped [bmim][PF_6] membrane. The longer solid line is this baseline data set; the shorter solid line is for the undoped [bmim][PF_6] membrane under humid conditions.

Consider the fluxes at 10 kPa of carbon dioxide for the four test conditions reported in Figure 8. Under non-humid conditions, the DiAPS/[bmim][PF_6] membrane had a flux that was 58% of the baseline flux rate; however, under humid conditions, the DiAPS/[bmim][PF_6] membrane performed 43% better than the baseline non-humid case (30% better than the humid, undoped case). Thus, the addition of humidity to the test conditions improved the transport of carbon dioxide through the DiAPS/[bmim][PF_6] membrane by 250%, relative to its non-humid test condition at 10 kPa of carbon dioxide driving force.

Comparing the DiAPS/[bmim][PF_6] membrane to the undoped [bmim][PF_6] membrane under humid conditions, Figure 8 shows that the addition of DiAPS to the liquid membrane does facilitate the transport of carbon dioxide. The Facilitation Factor is the ratio of flux with the mobile carrier to flux without a mobile carrier in an otherwise identical membrane. The Facilitation Factor for DiAPS ranges from 1.2 (at 19 kPa) to 1.8 (at 4.6 kPa). These Facilitation Factors are small, but are a "proof-of-concept" that facilitated transport is possible in RTIL Membranes.

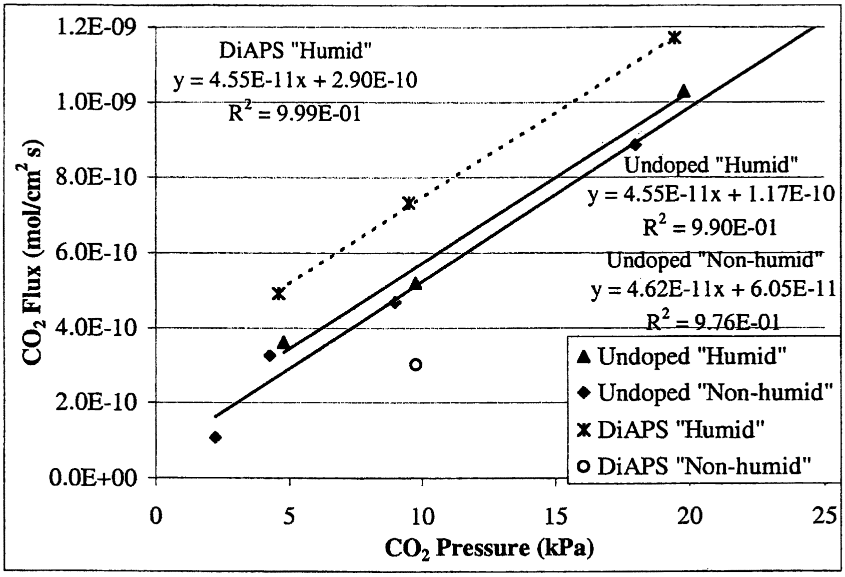

Figure 8. Ionic carrier-facilitated CO_2 flux from air or nitrogen for [bmim][PF_6] membranes. The carrier concentration in [bmim][PF_6] was 0.15 mole fraction DiAPS. Similar slopes are a characteristic of facilitated transport. Non-humid flux conditions are membranes in equilibrium with room air; humid flux conditions are membranes in equilibrium with water saturated air.

Humid Conditions

Why is facilitated transport only seen under humid conditions for primary and secondary amines? The water content of undoped [bmim][PF_6] is 11700 ppm (equilibrated with water, i.e. "humid" conditions) or 590 ppm (after a drying procedure) (*11*). While eq. 5 shows that water is necessary for the formation of carbamates from tertiary amines, eq. 6 for primary and secondary amines does not include water. However, primary and secondary amines can also utilize water in binding reactions with carbon dioxide (*10*):

$$CO_2 + 2R_2NH \Leftrightarrow R_2NH_2^+ + R_2NCOO^- \qquad (6)$$

$$CO_2 + R_2NH + \mathbf{H_2O} \Leftrightarrow R_2NH_2^+ + HCO_3^- \qquad (7)$$

$$CO_2 + R_2NCOO^- + \mathbf{2H_2O} \Leftrightarrow R_2NH_2^+ + 2HCO_3^- \qquad (8)$$

Therefore, the increased presence of water gives additional pathways for carbon dioxide binding as bicarbonate and carbamate. Note that subtraction of eq. 8 from

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2 times eq. 7 gives eq. 6. It is also worth noting that the bulk of studies on carbamate formation, to date, have used aqueous conditions that may have masked the role of water in carbamate formation. Alternatively, DiAPS adds bromide to the [bmim][PF_6] membrane in addition to amines. The hydroscopic nature of Br^- may increase the water content of the [bmim][PF_6] membrane under humid conditions compared to the undoped [bmim][PF_6] membrane. For this alternative hypothesis, water is the facilitated transport carrier of carbon dioxide via bicarbonate. Further studies are needed to examine the role of water in the transport of carbon dioxide in [bmim][PF_6] membranes.

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Improvements

Assuming that the facilitated transport shown in Figure 8 is from carbamate formation, the following could enhance the Facilitation Factor:

- Smaller DiAPS cations (with fewer phenyl groups) for higher diffusivity of the bound CO_2/Carrier
- Lower viscosity RTILs for higher diffusivity of the bound CO_2/Carrier
- Functionalized RTILs

The first two possibilities consider that transport, through a liquid membrane, is not just a function of the transporting chemical's combined solubility (physical solubility plus bound species) in the liquid, but also is a function of the time for the absorbed chemical to diffuse through the membrane. Since diffusion in a liquid is inversely related to the size of the diffusing species and the viscosity of the bulk fluid, any reduction in these two factors will increase the facilitated transport in RTIL membranes. The third possibility considers that a membrane composed of an amine functionalized RTIL would have an amine mole fraction much greater than the 0.15 reported in Figure 8. The higher the mole fraction of the carrier, the greater the quantity of bound chemicals for transport.

Conclusions

The work reported in this chapter has demonstrated the following for membrane separations with RTIL membranes:

- RTILs can be formed into thin film membranes for separation processes
- Performance of RTIL membranes is competitive with existing membrane materials
- Facilitated transport in RTIL membranes is possible

Furthermore, RTIL membranes (SILMs) combine the advantages of RTILs and supported liquid membranes (SLMs) in a manner that eliminates the disadvantages of existing SLMs for the following reasons:

- RTIL membranes have no measurable vapor pressure; so a SILM will have negligible loss of solvent via vaporization. *This is a disadvantage in current SLMs.*
- Adjusting properties of the RTILs should make dissolution of the solvent into liquid contacting phases negligible.
- Complexing agents incorporated into the RTIL will produce higher loadings than in traditional solvents with less chance for exchange with the contacting phase. *The result would be stable membranes with higher fluxes than existing SLMs.*
- The ability to produce "designer solvent systems" in the RTILs gives the potential to produce *millions* of separation specific membranes.
- RTILs possess the potential for producing highly selective membranes with high fluxes in comparison to polymer membranes.

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Potential for Future Research and Development

The proof-of-concept of RTIL membranes presented in this chapter opens up a broad range of possible future developments in membrane science. The potential exists for RTIL membrane development for gas separations, liquid separations, and even membrane reactors. For this reason, we feel that RTIL membranes are a “new class” of membranes. The development of RTIL membranes for the following gas separations could proceed by drawing directly on the work reported in this chapter:

- CO_2/air
- SO_2/air
- VOCs/air

However, we also plan to extend the development of RTIL membranes into liquid separations by studying organic separations from water and the dewatering of organic solvents. Finally, the chemical and thermal stability of RTILs combined with non-polymer porous membranes (such as metal and ceramic membranes) could lead to the development of membranes for harsh environmental conditions. Membrane science currently has only a limited number of membrane materials that can operate at high temperatures or under acid conditions.

Acknowledgements

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Chapter 7

Ionic Liquids: Solvents for the Twenty-First Century

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With the rapid growth in the number of publications relating to ionic liquids, this review describes recent developments in this area of study. Particularly, reference has been paid to clean synthesis and improving current methodology used in chemical synthesis.

Introduction

In the 19th Century, most ionic liquid chemistry was associated with the study of volcanic lava and cryolite. For all but the last few years of the 20th Century, the majority of ionic liquid research concentrated on high temperature molten salts, and on electrochemical uses of salts. But in the last few years of the 20th Century to the present date, there has been an eruption of publications in this field of research. In this review, the latest developments in reaction chemistry in ionic liquids are presented. A brief glance at the reference section of this review is testimony to the rapid growth of organic chemistry in ionic liquids. The number of publications appears to be growing exponentially (*1*). This rapidly expanding field of research has been reviewed by a number of authors, including Welton (*2*), Holbrey (*3*), Earle (*4*), Rooney (*5*), Seddon (*6*), Wasserscheid (*7*), and Dupont (*8*).

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

The term "Designer Solvents" has been applied to ionic liquids (*9*). To many chemists, performing reactions in ionic liquids may seem daunting and the range of ionic liquids or potential ionic liquids available is very large. However, many scientists have found that performing reactions in ionic liquids is straightforward and practical, compared with similar reactions in conventional organic solvents. This is particularly the case when considering reactions normally carried out in noxious and difficult to remove solvents such as dipolar aprotic solvents like dimethylsulfoxide.

Freemantle (*9*) has described ionic liquids as "designer solvents", of which properties can be adjusted to suit the requirements of a particular process. By making changes to the structure of either the anion, or the cation, or both, properties such as solubility, density, refractive index and viscosity can be adjusted to suit requirements (*10,11*). This behaviour can be of substantial benefit when carrying out solvent extractions or product separations, as the relative solubilities of the ionic and extraction phase can be adjusted to assist with the separation (*12*). Also, separation of the products can be achieved by other means such as distillation (usually under vacuum), steam distillation and supercritical fluid extraction.

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Reactions In Chloroaluminate(III) Ionic Liquids

The chemical behaviour of Franklin acidic chloroaluminate(III) ionic liquids (where $X(\mathrm{AlCl_3}) > 0.50$) (*6*) is that of a powerful Lewis acid. As might be expected, it catalyses reactions that are conventionally catalysed by aluminium(III) chloride, without suffering the disadvantage of the low solubility of aluminium(III) chloride in many solvents. These ionic liquids are straightforward to prepare and are made by mixing the appropriate organic halide salt with aluminium(III) chloride. It should be noted that these chloroaluminate(III) ionic liquids are very moisture sensitive and their synthesis and use must be performed in an inert atmosphere.

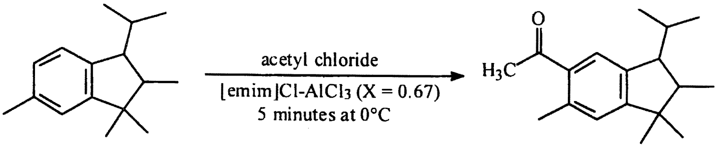

Figure 1. The acetylation of 1,1,2,6-tetramethyl-3-isopropylindane in [emim]Cl-AlCl$_3$ (X = 0.67) (13).

A classical reaction catalysed or promoted by Lewis acids is the Friedel-Crafts reaction, which was found to work efficiently in chloroaluminate(III) ionic liquids. A number of commercially important fragrance molecules have been

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synthesised by Friedel-Crafts acylation reactions in these ionic liquids. Traseolide® (5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane) (Figure 1) has been made in high yield in the ionic liquid [emim]Cl-$AlCl_3$ ($X = 0.67$) ([emim] = 1-ethyl-3-methylimidazolium). For the acylation of naphthalene, the ionic liquid gives the highest reported selectivity for the 1-position (*13*). The acetylation of anthracene at 0 °C was found to be a reversible reaction. The initial product of the reaction of acetyl chloride (1.1 equivalents) with anthracene is 9-acetylanthracene, formed in 70 % yield in less than 5 minutes. The 9-acetylanthracene was then found to undergo diacetylation reactions, giving the 1,5- and 1,8-diacetylanthracene and anthracene after 24 hours (*13*).

The benzoylation of aromatic compounds in ionic liquids was performed using benzotrichloride, which on aqueous work up gave ketones (*14*). The alkylation of a number of aromatic compounds by the use of a chloroaluminate(III) ionic liquid on a solid support has been investigated by Hölderich *et al.* (*15*). Here the alkylation of aromatic compounds such as benzene, toluene, naphthalene and phenol with dodecene was performed using the ionic liquid [bmim]Cl-$AlCl_3$ ([bmim] = 1-butyl-3-methylimidazolium) supported on silica, alumina and zirconia. With benzene, monoalkylated dodecylbenzenes were obtained (*15*).

Cracking and isomerisation reactions occur readily in acidic chloroaluminate(III) ionic liquids. A remarkable example of this is the reaction of polyethylene, which is converted to a mixture of gaseous alkanes with the formula (C_nH_{2n+2}, where $n = 3$-5) and cyclic alkanes with a hydrogen to carbon ratio of less than two (Figure 2) (*16*).

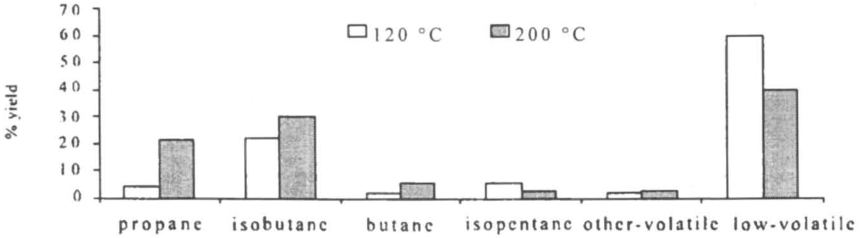

Figure 2. The products from the ionic liquid cracking of high-density polyethylene (n = 5000) at 120 °C and 200 °C (16).

The distribution of the products obtained from this reaction depends upon the reaction temperature (Figure 2) and differs from other polyethylene recycling reactions in that aromatics and alkenes are not formed in significant concentrations. Another significant difference is that this ionic liquid reaction occurs at temperatures as low as 90 °C, whereas conventional catalytic reactions require much higher temperatures, typically 300-1000 °C (*15*). SECR Defense has reported a similar cracking reaction for lower molecular weight hydrocarbons in chloroaluminate(III) ionic liquids (*17*). A similar reaction occurs with fatty acids (such as stearic acid) or methyl stearate, which undergo isomerisation, cracking, dimerisation, and oligomerisation reactions. This has been used to convert solid stearic acid into the more valuable liquid isostearic acid (*18*). The isomerisation and dimerisation of oleic acid and methyl oleate have also been found to occur in chloroaluminate(III) ionic liquids (*19*). The dimerisation and oligomerisation of olefins in the presence of homogeneous nickel(II) catalysts have been studied extensively in chloroaluminate(III) and alkylchloroaluminate(III) ionic liquids (*20,21*). Few catalysts are known that catalyse the linear dimerisation and oligomerisation of C_4-olefins. Linear C_8-olefin dimers are highly desirable intermediates for the production of C_9-plasticizers, exhibiting better thermal properties than those produced from highly branched C_8-olefin dimer feedstock. This has been developed commercially in the IFP Difasol process (*1*). The products of these reactions are insoluble in the ionic liquid and can be separated by decantation, leaving the ionic liquid and catalyst behind and hence the catalyst and solvent can be reused.

Polycyclic aromatic hydrocarbons dissolve in chloroaluminate(III) ionic liquids. The addition of a reducing agent such as an electropositive metal and a proton source results in the selective hydrogenation of the aromatic compound. For example pyrene and anthracene can be reduced to perhydropyrene and perhydroanthracene at ambient temperatures and pressures (Figure 3). Interestingly, only the thermodynamically most stable isomer of the product is obtained (*22*). This contrasts with catalytic hydrogenation reactions, which require high temperatures and pressures and an expensive platinum oxide catalyst and give rise to an isomeric mixture of products.

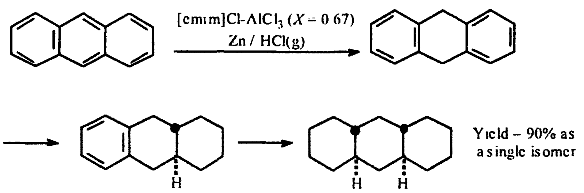

Figure 3. The reduction of anthracene to perhydroanthracene (22).

Other recently reported reactions include hydrogenation reactions of cyclohexene using Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, in basic chloroaluminate(III) ionic liquids (*23*). Chloroaluminate(III) ionic liquids have recently been used for a number of other reaction types. One example is in the acylative cleavage of ethers. Singer *et al.* have shown that benzoyl chloride reacts with diethyl ether to give ethyl benzoate (*24*). Another common reaction

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is the chlorination of alkenes to give dihaloalkanes. Patell *et al*. have reported that the addition of chlorine to ethene in acidic chloroaluminate(III) ionic liquids gave 1,2-dichloroethane (*25*). Also, esterification (*26,27*) and aromatic alkylation reactions (*28*) have appeared in the patent literature.

Neutral Ionic Liquids

Chloroaluminate(III) ionic liquids are excellent catalysts and solvents in many processes, but suffer from several disadvantages, such as their moisture sensitivity and the difficulty of separation of products containing heteroatoms. Hence research is shifting to the investigation of ionic liquids that are stable to water. This allows for straightforward product separation and ease of handling. In particular, a number of ionic liquids have been found to be hydrophobic (immiscible with water), but readily dissolve many organic molecules (with the exception of alkanes, and some ethers and alkylated aromatic compounds such as toluene). An example of this is the ionic liquid [bmim][PF_6] (*29*), which forms triphasic solutions with alkanes and water (*30*).

This multiphasic behaviour has important implications for clean synthesis and is analogous to the use of fluorous phases in some chemical processes (*31*). For example, transition metal catalysts can be exclusively dissolved in the ionic liquid. This allows products and by-products to be separated from the ionic liquid by solvent extraction with either water or an organic solvent. This is of key importance when using precious metal catalysts or catalysts with expensive ligands, enabling both the ionic liquid and catalyst to be recycled and reused.

Rogers and coworkers have studied the liquid-liquid extraction of various aromatic compounds between water and [bmim][PF_6], at different values of pH (*29*). This has also been extended to the use of task-specific ionic liquids for the extraction of metal ions from aqueous solution (*32,33*). Alternatively, some volatile products can be separated from the ionic liquid and catalyst by distillation. This is because the ionic liquid has effectively no vapour pressure and therefore cannot be lost. There also exists the possibility of extraction with supercritical solvents. A recent example is the use of supercritical carbon dioxide to extract naphthalene from [bmim][PF_6] (*34,35*). A more extensive study of the behaviour of a range of ionic liquids with high pressure CO_2 has been reported by Brennecke (*36*). The addition of CO_2 only causes a modest expansion of the ionic liquid, compared with organic solvents. This scCO_2 / [bmim][PF_6] system has been used in the synthesis on *N,N*-dialkylformamides from CO_2, H_2 and a dialkylamine and in the hydrogenation of alkenes (*37*). The behaviour of CO_2 / [bmim][PF_6] and [bmim][BF_4] have been investigated in ATR-IR study (*38*), and the authors have speculated as to the nature of the CO_2 - ionic liquid interactions.

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Catalysis in Neutral Ionic Liquids

Chauvin *et al.* developed the first hydroformylation reactions of alkenes in ionic liquids (*39,40*). Recently, Wasserscheid (*41*) has investigated the hydroformylation of alkenes such as octene and methyl pent-3-enoate in a $SnCl_2$-[4-MBP]Cl ([4-MBP] = 4-methyl-1-butylpyridinium) binary ionic liquid using platinum catalysts. This was extended to the neutral ionic liquid [bmim][PF_6] with a rhodium catalyst containing a novel cobaltacenium ligand (*42*) as shown in Figure 4. High *n:iso* ratios were obtained with this system and with a similar system based in a phenylguanidinium modified xanthene ligands (*43*). Cole-Hamilton has developed a continuous flow hydroformylation reaction of oct-1-ene, using supercritical CO_2 as the extraction solvent. This process has been performed on the pilot plant scale (*44*).

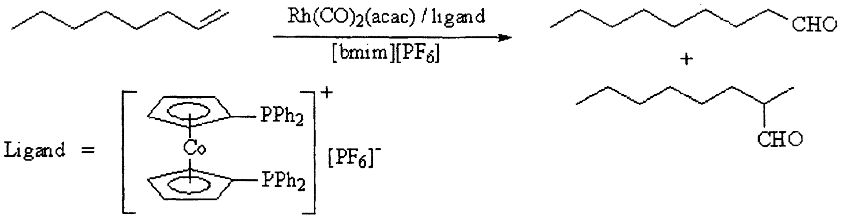

Figure 4. The hydroformylation of an oct-1-ene in [bmim][PF_6] (42).

Neutral ionic liquids such as [bmim][PF_6] have also been found to be excellent solvents for the Diels-Alder reaction (*45,46*). The reactions in ionic liquids are marginally faster than in water and are considerably faster than in the organic solvent diethyl ether. The selectivities of the various isomers in this reaction can be improved from 4 : 1 to 20 : 1 by the addition of a mild Lewis acid such as zinc(II) iodide to the ionic liquid [bmim][PF_6]. One of the key benefits of this is that the ionic liquid and catalyst can be recycled and reused after solvent extraction or direct distillation of the product from the ionic liquid. The use of phosphonium tosylates have also been reported for this reaction (*47*), but these salts have higher melting points that most ionic liquids in common use. A new class of room temperature ionic liquids based on phosphonium salts is introduced in an earlier chapter of this book (*48*). The reaction has also been carried out in chloroaluminate(III) ionic liquids, but the moisture sensitivity of these systems is a major disadvantage (*49*).

The Lewis acid in ionic liquid methodology has also been used for Friedel-Crafts alkylation reactions. Song (*50*) has reported that scandium(III) triflate in [bmim][PF_6] acts as an alkylation catalyst in the reaction of benzene with hex-1-

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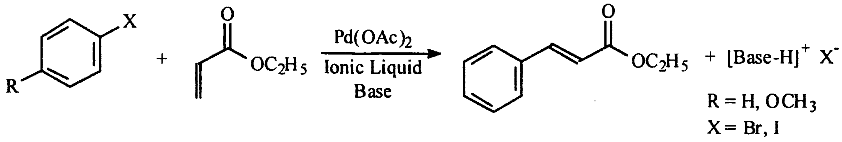

Figure 5. The Heck reactions of aryl halides in ionic liquids (30).

ene. Also Raston has reported an acid catalysed Friedel-Crafts reaction (*51*) where 3,4-dimethoxyphenylmethanol was cyclised to cyclotriveratrylene.

One of the most promising areas of ionic liquid chemistry is as media for metal catalysed coupling reactions such as the Heck reaction. Hermann has provided an excellent review of C-C coupling reactions in ionic liquids (*52*). It has been found that many palladium complexes dissolve in ionic liquids (*53*) and allow the products and by-products of the Heck reaction to be extracted with either water or alkane solvents (*30*) (Figure 5). Also, separation of the products by distillation directly from the ionic liquid / catalyst is feasible where the products and by-products are volatile. This allows the expensive catalyst to be easily recycled as it remains in the ionic phase. This differs from conventional Heck reactions, in which the catalyst is usually lost at the end of the reaction, and also noxious dipolar aprotic solvents such as DMF are required. An alternate Heck reaction in ionic liquids uses aromatic anhydrides as a source of the aryl group. This has the advantage that the by-product of the reaction is an arylcarboxylic acid (which can readily be converted back to the anhydride) and that halide-containing waste is not formed (*30*).

Two types of ionic liquid / catalyst combinations were found to be effective, the first being based on chloride salts. A combination of *N*-hexylpyridinium chloride ($[C_6py]Cl$) and palladium(II) acetate was found to be one of the most effective combinations. Here, the palladium(II) acetate interacts with the ionic liquid to form $[C_6py]_2[PdCl_4]$ (*30*), which is thought to be the catalytic species. The second system was a 1-alkyl-3-methylimidazolium hexafluorophosphate (V) or tetrafluoroborate(III) ionic liquid combined with palladium(II) acetate / Group 15 ligand catalyst. The ligand is needed to prevent the formation of imidazolylidine complexes with the palladium catalyst. The structures of these palladium carbene complexes have been reported by several authors (*53,54*) and some have also been found to be catalytically active in the Heck reaction (*55*). Similar findings were subsequently reported by Howarth in the reaction of 4-bromoanisole with alkyl acrylates, and confirmed that $[bmim][PF_6]$ could be used as a replacement for DMF (*56*). The preparation of aryl ketones by the Heck reaction of aryl halides with vinyl ethers was investigated by Xiao and coworkers. (*57*) (Figure 6).

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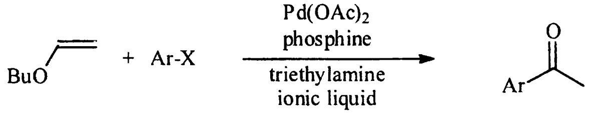
BuO
+ Ar-X
Pd(OAc)2
phosphine
triethylamine
ionic liquid
O
Ar

Figure 6. The palladium catalysed arylation of vinyl ethers (56).

Reactions that have been found to proceed under similar conditions include palladium catalysed allylation and amination reactions in [bmim][BF$_4$] (*58*). The palladium catalysed alkoxycarbonylation of bromobenzene and iodobenzene with CO in [bmim][PF$_6$] and [bmim][BF$_4$] have been investigated by Tanaka and coworkers (*59*). Arylcarboxylates were obtained in excellent yields, and it was found that the catalyst and ionic liquid system could be recycled and reused. The palladium catalysed allylic alkylation of dimethyl malonate by 3-acetoxy-1,3-diphenylprop-1-ene have been investigated by Xiao and coworkers. (*60*) Here, the effect of various phosphine ligands on the yield and rate of reaction were studied for reactions carried out in the ionic liquid [bmim][BF$_4$]. This reaction was further developed by Toma *et al.* who used a chiral palladium catalyst (*61*) to obtain the product (Figure 7) in moderate enantioselectivities.

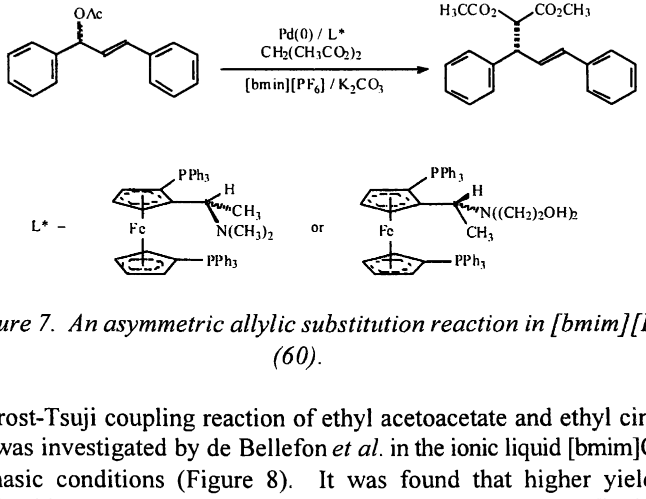
OAc
Pd(0) / L*
CH2(CH3CO2)2
[bmin][PF6] / K2CO3
H3CCO2
CO2CH3
L* -
PPh3
H
CH3
Fc
N(CH3)2
PPh3
or
PPh3
H
N((CH2)2OH)2
Fc
CH3
PPh3

Figure 7. An asymmetric allylic substitution reaction in [bmim][PF$_6$] (60).

The Trost-Tsuji coupling reaction of ethyl acetoacetate and ethyl cinnamyl carbonate was investigated by de Bellefon *et al.* in the ionic liquid [bmim]Cl (*62*), under biphasic conditions (Figure 8). It was found that higher yields and considerably higher turnover numbers were obtained in the [bmim]Cl / methylcyclohexane solvent combination than with pentanenitrile / water system.

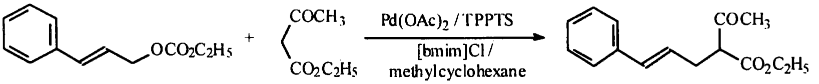
OCO2C2H5
+
COCH3
CO2C2H5
Pd(OAc)2 / TPPTS
[bmim]Cl /
methylcyclohexane
COCH3
CO2C2H5

Figure 8. The Trost-Tsuji coupling in biphasic conditions (61).

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Welton and coworkers have reported the Suzuki coupling of aryl halides with aryl boronates, (*63*) and the related Stille coupling of vinyliodides with aryl stannanes in [bmim][BF_4] had been carried out by Handy and Zang (Figure 9) (*64*). Howarth *et al.* have achieved the coupling of aryl halides with a catalyst made *in situ* from zinc and $(Ph_3P)_2NiCl_2$ in the ionic liquid [bmim][PF_6] (*65*).

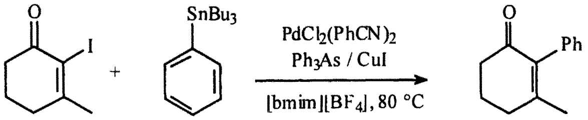

Figure 9. The Stille Coupling in [bmim][BF_4] (63).

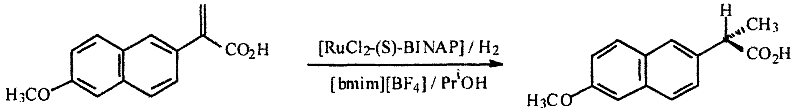

Figure 10. The synthesis of (S)-Naproxen in [bmim][BF_4] (68).

Neutral ionic liquids have been extensively studied as solvents for hydrogenation reactions. Examples of this include the hydrogenation of cyclohexene (*66*), and the complete hydrogenation of benzene rings (*67*). Dupont *et al.* have used the ionic liquids [bmim][BF_4] and [bmim][PF_6] in the selective palladium acetoacetate catalysed hydrogenation of dienes to monoenes (*68*). Recently, asymmetric hydrogenation reactions have appeared. An example is in the synthesis of (S)-Naproxen (Figure 10) in the ionic liquid [bmim][BF_4] (*69*). The cyclodimerisation of 1,3-dienes using an iron nitrosyl catalyst has been performed by Souza and coworkers (*70*), in [bmim][PF_6] and [bmim][BF_4]. The products of the reaction (formed in quantitative yield) are insoluble in the ionic liquid / catalyst, and can be isolated by phase separation.

Two reports of epoxidation reactions in ionic liquids have been presented. Abu-Omar has used [emim][BF_4] as the solvent in the methyltrioxorhenium(VII) catalysed epoxidation of alkenes with urea hydrogen peroxide (*71*). Several advantages of this include homogeneous reaction conditions, and the ionic liquid being a non-aqueous medium, no diol is formed. The use of Jacobsen's catalyst for the epoxidation of various alkenes have been carried out in [bmim][PF_6] by Song *et al.* (*72*). Enantioselectivities between 84 and 96 % were obtained and it was found that the catalyst and ionic liquid could be reused over at least 5 reaction cycles. Beckmann rearrangements of several ketoximes were performed in the room temperature ionic liquid based on 1,3-dialkylimidazolium or alkylpyridinium salts containing phosphonated (*e.g.* P_2O_5) compounds were performed by Deng *et al.* (*73*).

Non-catalytic reactions in ionic liquids

A number of nitration reactions have been carried out by Laali *et al.* (*74*). The reactions of nitrates, preformed nitronium salts and alkyl nitrates with aromatic compounds were performed in a wide range of ionic liquids. The first examples of a Horner-Wadsworth-Emmons reactions have been given by Tanaka and coworkers (*75*). Here the ionic liquid 8ethyl-1,8-diazabicyclo[5,4,0]-7-undecene trifluoromethanesulfonate [EtDBU][OTf], has been used in the synthesis of α-fluoro-α,β-unsaturated esters.

One of the most common reactions in organic synthesis is the nucleophilic displacement reaction. Indole and 2-naphthol undergo alkylation on the nitrogen and oxygen atoms respectively (Figure 11), when treated with an alkyl halide and base (usually NaOH or KOH) in [bmim][PF_6] (*76*). These reactions occur with similar rates to those carried out in dipolar aprotic solvents such as DMF or DMSO. The by-product (sodium or potassium halide) of the reaction can be extracted with water and the ionic liquid recycled. A quantitative study of the nucleophilic displacement reaction of benzoyl chloride with cyanide ion in [bmim][PF_6] was investigated by Eckert and coworkers (*77*). The separation of the product 1-phenylpropionitrile from the ionic liquid was reported by distillation and with supercritical CO_2.

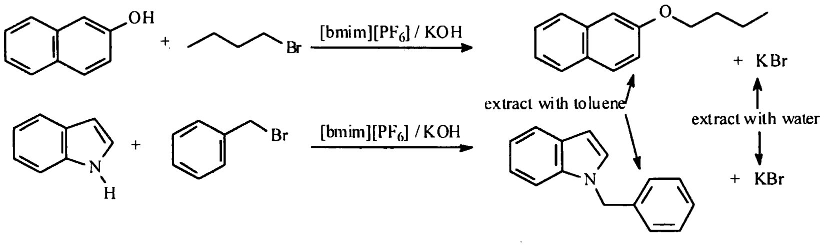

Figure 11. Alkylation reactions in [bmim][PF_6] (75).

As a demonstration of the complete synthesis of a pharmaceutical in an ionic liquid, Pravadoline was selectedas it combines a Friedel-Crafts reaction and a nucleophilic displacement reaction (Figure 12) (*78*). The alkylation of 2-methylindole with 1-(*N*-morpholino)-2-chloroethane occurs readily in [bmim][PF_6] and [bdmim][PF_6], in 95-99% yields respectively, using potassium hydroxide as the base. The Friedel-Crafts acylation step in [bmim][PF_6] at 150 °C occurs in 95% yield and requires no catalyst.

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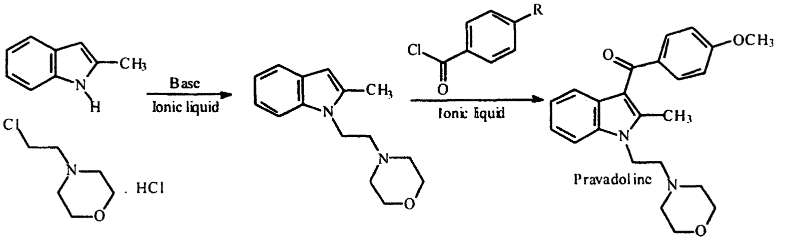

Figure 12. The complete synthesis of Pravadoline in [bmim][PF$_6$] (77).

The addition of organometallic reagents to carbonyl compounds is an important reaction in organic chemistry, with the Grignard reaction being one example of this. Hence protocols that achieve similar results in ionic liquids are desirable. Gordon and McClusky (*79*) have reported the formation of homoallylic alcohols, from the addition of allyl stannanes to aldehydes in the ionic liquids [bmim][BF$_4$] and [bmim][PF$_6$] (Figure 13). It was found that the ionic liquid could be recycled and reused over several reaction cycles. Kitazume and Kasai found that the Reformatsky reaction gave moderate to good yields ionic liquids such as [EtDBU][OTf] (*80*). Here the reactions of ethyl bromoacetate and ethyl bromodifluoroacetate with benzaldehyde and zinc gave the expected product in 45-95 % yield. The reactions of aldehydes with alkynes to give propargyl alcohols is also described.

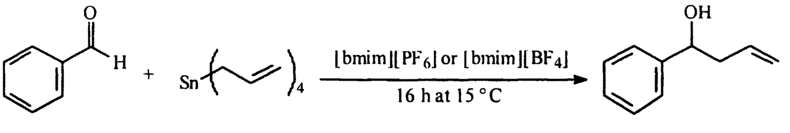

Figure 13. Allylation of aldehydes in [bmim][PF$_6$] or [bmim][BF$_4$] (78).

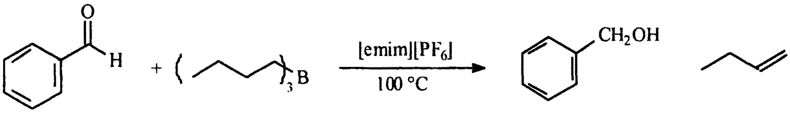

Figure 14. The reduction of benzaldehyde in [emim][PF$_6$] (81).

McCluskey *et al.* have also used [bmim][BF$_4$] as a solvent for the allylation of aldehydes and Weinreb amides (*81*). Similar selectivities and similar or slightly lower yields were obtained in this ionic liquid, compared with reactions carried out in methanol. Ionic liquids such as [bmim][BF$_4$] and [emim][PF$_6$] have been used in the trialkylborane reduction of aldehydes to alcohols (Figure 14) (*82*).

Bio-transformations and biological applications

A surprising use of ionic liquids is in the field of bio-transformations (*83*). Room temperature ionic liquids, such as [bmim][PF_6], have been used as direct replacements for conventional organic solvents in multiphase bioprocess operations. Examples include the liquid-liquid extraction of the antibiotic erythromycin and two-phase bio-transformation processes (*84*), the synthesis of Aspartime(*85*), and alcoholysis, ammoniolysis, and perhydrolysis reactions (*86*). Meagher *et al.* have used the ionic liquid [C_8-mim][PF_6] in the recovery of butanol (a product of a fermentation of carbohydrates) from an aqueous solution of butanol. The butanol was separated from the ionic liquid by a process knows as pervapouration (*87*). The first lipase catalysed kinetic resolution has been reported by Wasserscheid (*88*). Two papers have appeared linking ionic liquids with DNA research. Thorp *et al.* have produced an intriguing report of the first salts using DNA in the anion of an ionic liquid (*89*). An example is a binary salt of [Co(MePEG-bpy)$_3$'DNA]-[Fe(MePEG-bpy)$_3$][ClO_4]$_2$ ($X = 0.5$). Secondly, with a view to synthesizing DNA based polymer electrolytes, the conductivities of films made from mixtures of ionic liquids have been made and investigated (*90*).

Miscellaneous related publications

Gordon has carried out an investigation of ionic liquids for photochemical applications. Here [bmim][PF_6] has been used as the solvent in the study of photoelectron transfer reactions between [Ru(bpy)$_3$]$^{2+}$ and methyl viologen (MV^{2+}) (*91*). A novel use of the salt [bmim][PF_6] is to enhance microwave absorption and hence accelerate the rate of a reaction. Ley found that [bmim][PF_6] enhanced the rate of the microwave promoted thionation of amides using a polymer supported thionating agent (*92*). Hardacre *et al.* have developed a protocol for the synthesis of deuterated imidazoles and imidazolium salts (*93*). The procedure involves the platinum- or palladium-catalysed deuterium exchange of d^3-methylimidazole with D_2O, followed by reaction with a deuterated alkyl halide. Three papers have appeared recently discussing the "polarity" of ionic liquids. The techniques involve the use of solvochromatic dyes (*94,95*) or fluorescent probes (*96*). Although it is hard to generalise, those tested display polarities similar to short chain *n*-alcohols.

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Conclusion

The range of chemical reactions that can be performed in ionic liquids has grown rapidly in the last few years. The use of chloroaluminate(III) ionic liquids is being superceded by neutral ionic liquids, due to their moisture stability and the ease with which they can be recycled. The reactions that can be carried out in ionic liquids now cover most of the classes of reactions that can be performed in conventional solvents. One of the key trends has been to use ionic liquids as a medium for a catalyst, and after the reaction has been performed, to separate the ionic liquid and catalyst from the products of the reaction and thus allow the ionic liquid and catalyst to be recovered.

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Chapter 8

Preparation of Functional Silica Aerogels Using Ionic Liquids as Solvents

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Abstract

A new methodology has been developed to prepare functional silica aerogels using ionic liquids. This methodology makes use of the unique solvent properties of ionic liquids (negligible vapor pressure and ionicity), allowing application of long aging times without macroscopic phase segregation between ionic liquids and the silica network. The long ambient aging time also ensures development of stable silica networks so that the ionic liquids can be extracted and dried without collapse of the silica network.

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

Introduction

The extraordinary properties of aerogels including high surface areas, low refractive indices, low dielectric constants, low thermal loss coefficients, and low sound velocities, lead to potential applications in areas such as ultra-low dielectric constant interlayer dielectrics, reflective and antireflective coatings, flat panel displays, sensors, catalyst supports, and sorbents.[1, 2, 3, 4] Thus far, the synthesis of silica-based aerogels has been accomplished mainly through the controlled condensation of small colloidal particles produced by sol-gel processing in alcoholic aqueous solutions, followed by a supercritical drying process. A highly desirable goal in aerogel synthesis is the elimination of the supercritical drying step, which is the most expensive and risky aspect of the process. The ambient-pressure route enables the preparation of aerogel materials in a continuous process, which was previously impossible within the constraints of a supercritical autoclave. We have recently developed a new process to synthesize aerogels using ionic liquids as solvents.[5] This ambient process makes use of the unique properties of ionic liquids, allowing the synthesis of stable silica aerogels without use of the supercritical drying step. The key properties of ionic liquids used in our study are (1) negligible vapor pressure and (2) ionicity.[6, 7, 8, 9, 10, 11, 12, 13, 14, 15] The former attribute allows a long aging process to be applied in synthesis without concern about shrinkage of the network due to the vaporization of solvents, while the latter ensures that no phase separation between silica polymers and solvents. In the work reported here, we have extended our methodology to synthesize silica aerogels containing functional ligands. This new type of functional aerogels may find potential application as advanced sorbents.

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Experimental

Synthesis: Functional aerogels were prepared by the sol-gel process using a room-temperature ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ($BuMeIM^+BF_4^-$), which was prepared by the metathesis of 1-butyl-3-methylimidazolium chloride ($BuMeIM^+Cl^-$) and $NaBF_4$.[16, 17] Various mixtures of aminopropyltrimethoxylsilane [$(MeO)_3Si(CH_2)_3NH_2$ = APTS, Aldrich] and tetramethylorthosilicate [$Si(OM)_4$ = TMOS, Aldrich] were used as sol-gel precursors. The acid-catalyzed sol-gel process using formic acid (FA) was employed in the aerogel preparation.[5] In a typical run, TMOS, APTS, FA, and $BuMeIM^+BF_4^-$ were mixed in a plastic bottle. **Table 1** gives the conditions for the preparation and the ratios of precursor solutions. In all cases, a monolithic gel was formed. The gelation times were all less than 1 min. The resulting gels were cured at ambient temperature for 2 weeks in open air. Then, the entrapped ionic liquids were extracted by acetonitrile (Baker Chemical Co., HPLC grade) at reflux for 1 week. All the functional aerogels were dried in a vacuum oven at 40°C. The final products were translucent.

Characterization: FTIR spectra were recorded on a Bio-Rad FTS 3000 FTIR spectrophotometer. Nitrogen adsorption isotherms were measured with a Micromeritics Gemini 2375 surface area analyzer. The small-angle X-ray scattering (SAXS) measurements were conducted using the 5-m SAXS camera at the SAXS user facility of the Oak Ridge National Laboratory.

Table 1. Compositions of precursor solutions and gelation times.

Sample	*TMOS (mmol)*	*APTS (mmol)*	*FA (mmol)*	*Ionic liquid (ml)*	*Gelation Time (min)*
0%[a]	6.72	0	53.0	1	<1
16%	6.72	1.14	53.0	1	<1
28%	6.72	2.29	53.0	1	<1
37%	6.72	3.42	53.0	1	<1
44%	6.72	4.56	53.0	1	<1
50%	6.72	5.7	53.0	1	<1

[a] weight percent of APTS in the mixture of TMOS and APTS.

Results and Discussion

As seen from **Table 1**, the gelation times for the sol-gel process using the ionic liquid were all less than 1 min. In order to determine the effect of the ionic liquid on gelation time, the same sol-gel processing was conducted without use of the ionic liquid. In the latter case, the gelation times were longer than 30 min. Accordingly, the ionic liquid plays an important role in accelerating sol-gel processes. This enhanced reaction rate can be rationalized by Hammond's postulate.[18] In general, sol-gel processes involve two types of

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exothermic reactions: (1) hydrolysis and (2) condensation. The intermediate products of both reactions are considered as charged species. These charged species should be well solvated by the corresponding conjugated ions of the ionic liquid but the active sites are not complexed by the solvent molecules because of the noncomplexing nature of the ionic liquid. Therefore, the ionic liquid stabilizes the intermediate products to a significantly greater extent than conventional solvents, resulting in shortened gelation times according to Hammond's postulate. The mechanism for aerogel formation in the ionic liquid involves initiation of the formation of sol particles by formic acid, which is followed by effective aggregation of the sol particles in the ionic liquid into a sol-gel network. Concurrently, the ionic liquid becomes entrapped in the growing covalent silica network, rather than being chemically bound to the inorganic matrix. A long aging time implemented before extraction of the nonvolatile ionic liquid further enhances the stability of the sol-gel network. No macroscopic phase separation between the gel and the ionic liquid solvent has been observed. The homogeneity is retained throughout the entire aging process, indicating that the interaction between the sol particles and the ionic liquids is favored thermodynamically. The ionic liquid forms a homogeneous solution with sol-gel precursors. If other solvents such as dimethyl sulfoxide (DMSO) are used in the sol-gel preparation, no appreciable pore volumes (<0.1 cm^3/g) are found. In fact, similar results have been reported in the literature concerning the doping of silica with organic liquids through sol-gel processes.[19]

Figure 1 presents FTIR spectra of the aerogels as a function of the ratio between TMOS and APTS. As seen from this figure, both the C-H stretching and the $-NH_2$ bending vibrational IR features resulting from APTS around 2900 cm^{-1} and 1500 cm^{-1} increase with APTS concentrations. Accordingly, the amine functional ligands are covalently bonded to the silica networks in the functional aerogels. **Figure 2** shows a comparison of FTIR spectra of a typical sol-gel sample before and after removal of the ionic liquid. The disappearance of the bands attributed to the ionic liquid indicates that most of the ionic liquid has been removed through extraction and vacuum drying. The structures of the resulting aerogels were investigated by making nitrogen sorption measurements. The adsorption isotherms have shapes similar to those expected for silica aerogels. Both BET surface areas and pore volumes (**Table 2**) decreased as the amount of APTS was increased. This observation is consistent with the trend observed for the functional aerogels prepared by the supercritical drying process. The decrease in the surface areas and the pore volumes can be attributed to the less stable structures induced by the functional ligands.

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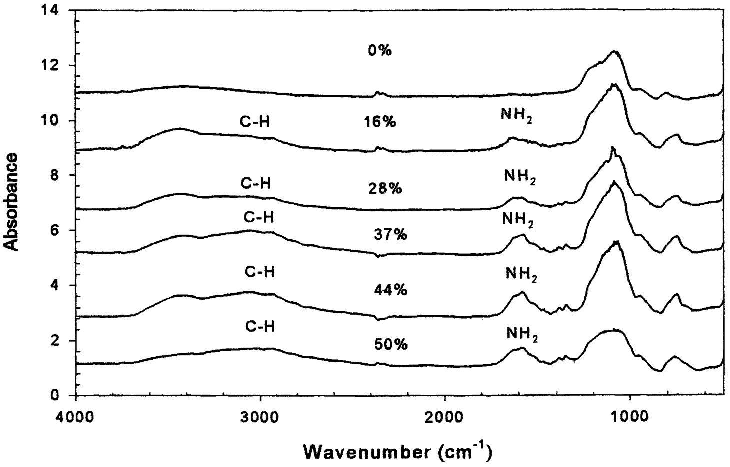

Figure 1 FTIR spectra as a function of APTS weight percent.

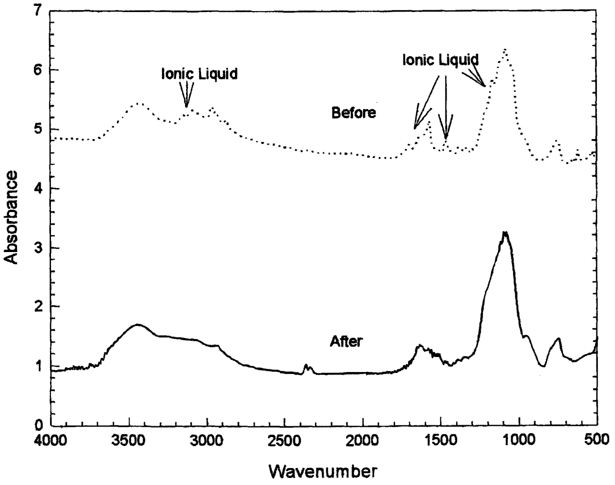

Figure 2 FTIR spectra of functional silica (16%) before and after extraction of the ionic liquid.

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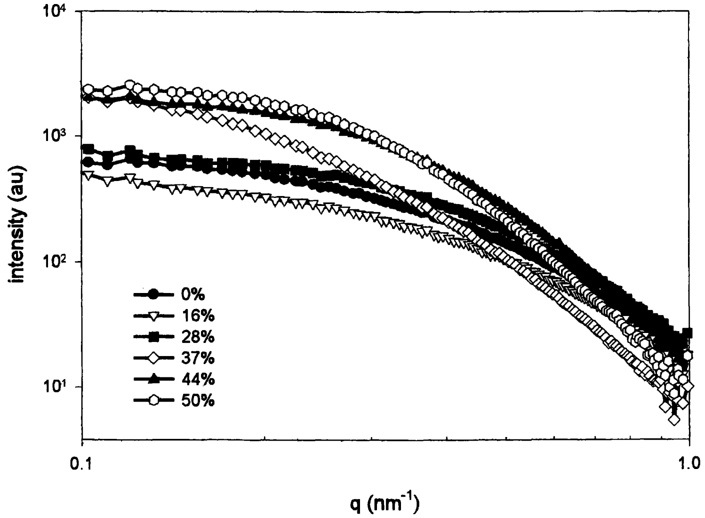

Figure 3 Small-angle X-ray scatterings of functional aerogels.

Table 2. Surface areas and total pore volumes

Sample	*Surface area* *m^2/g*	*Total pore volume* *cm^3/g*
0%	362.1	1.8810
16%	504.8	1.2552
28%	454.3	1.0507
37%	347.7	0.8484
44%	303.1	0.7121
50%	222.6	0.7200

The mesoscopic structures of our aerogels were also investigated by SAXS measurements. **Figure 3** shows the SAXS patterns as a function of APTS concentration. Scattering intensities at different Q ranges probe different structural features of aerogels.[20, 4] In the Porod range, the scattering intensity changes according to $I \propto q^{-D_m}$, where D_m is mass fractal dimension, which is a measure for the degree of branching of the network formed by the primary particles.[20] **Table 3** summarizes the values of R_g (radius of gyration) and mass fractal dimensions determined from SAXS measurements. All of our aerogel products exhibited a mass fractal structure whose dimension was below 2. This small fractal dimension indicates a highly porous sol-gel network and is consistent with the mass fractal dimension for aerogel materials.[3, 4] The increase of the mass fractal dimension with APTS concentration supports the results obtained through nitrogen adsorption measurements.

Table 3. Structural information obtained from SAXS measurements.

Sample	*Radius Gyration* R_g *(nm)*	*Mass Fractal dimension* D_m
0%	4.73	1.24
16%	4.45	1.26
28%	4.33	1.36
37%	5.37	1.65
44%	5.30	1.71
50%	5.91	1.87

In conclusion, we have extended our previous method[5] for the preparation of silica aerogels by using ionic liquids as solvents to synthesize functional aerogels. The structures of the resulting aerogel products have been characterized. Both the surface areas and the pore volumes are similar to those obtained for aerogels prepared by the supercritical drying process. Currently, we have extended this methodology further to prepare ordered mesoporous silica materials using 1,3-dialkylimidazolium cations with one of the alkyl-chain substituents lengthened.[21]

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Chapter 9

Homopolymerization and Block Copolymer Formation in Room-Temperature Ionic Liquids Using Conventional Free-Radical Initiators

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Free radical addition polymerization and copolymerization has been investigated in a range of room temperature ionic liquids (RTILs). We report results on synthesis of high molecular weight acrylic polymers in RTILs, as well as results on block copolymer formation via sequential monomer addition. The latter reactions take advantage of the long-lived nature of free radicals in some of these systems. Homopolymerization under conditions where the growing radicals precipitate in the RTIL leads to simultaneous rapid rates of polymerization and high molecular weights. This method shows great promise for economical and 'green' synthesis of polymers.

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

Introduction

Free radical polymerization is a key process for the polymer industry. Robust and economical, it accounts for about 50% of all mass-produced polymers (*1*). The study of free radical polymerization has been stimulated recently by the development of a variety of "living" free radical polymerization techniques (*2-4*). One of the major virtues of radical polymerization is its relative insensitivity to monomer and solvent impurities, as compared to ionic polymerization. Thus radical polymerization can be carried out under less rigorous conditions, resulting in reduced cost. Another advantage of this process is that it can be applied to an extremely broad range of monomers.

Almost all polymers made from conventional free radical processes are homopolymers and random copolymers. Conversely, block copolymers, composed of chemically different "blocks" covalently bonded together, offer potential to create complex and functional new nanostructured materials that were unimaginable just a few decades ago. Although many methods, including living anionic, cationic, and radical polymerization, are available to synthesize well-defined block copolymers, all of them, including living radical polymerization, require relatively demanding experimental procedures or else the compositions and/or structures of the final block copolymers are not well controlled. It has not been possible in general to make block copolymers through conventional free radical polymerization (*5*). Moreover, most conventional free radical polymerizations are done in volatile organic compound (VOC) solvents, which have been blamed for increasing air pollution.

In recent years, room temperature ionic liquids (RTILs) have emerged as promising substitutes for volatile organic solvents, and have attracted much interest from the chemistry community for their potential as green "designer solvents," and several excellent reviews are available (*6-11*). RTILs are salts that are liquid around room temperature (melting points as low as –96 °C). Invariably, these ionic liquids are either organic salts or mixtures consisting of at least one organic component. Cations are typically asymmetric and bulky (such as alkylammonium, alkylphosphonium, N-alkylpyridinium, and N, N'-dialkyimidazolium), which accounts for their low melting points. On the other hand, anions contribute more to the overall properties of the ionic liquids. Variations in cations and anions can produce a very large range of ionic liquids (*12*), thus allowing for fine-tuning of ionic liquid properties for specific applications. Constrained by high Coulombic forces, some RTILs exert negligible vapor pressure (i.e., are non-volatile) (*10*); they also may be non-flammable and thermally stable (*7*). RTILs not only show potential for use in separations (*13, 14*) and as electrolytes, but they are also promising solvents for

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chemical syntheses and particularly for catalysis, including applications in polymerization.

In the early 1990s, several polymerization studies were done in chloroaluminate based ionic liquids. Carlin and coworkers (*15*) investigated the electrochemistry of $TiCl_4$ in $AlCl_3$-1-ethyl-3-methylimidazolium chloride ([emim]) melt and they found the combination of $TiCl_4$ and $AlEtCl_2$ in $AlCl_3$-[emim]Cl to be catalytically active for ethylene polymerization. Even though the yield of polyethylene was very low, they demonstrated that an RTIL could serve as a polymerization medium. Using Cp_2TiCl_2 instead of $TiCl_4$, higher yields of polyethylene could be achieved as reported by Carlin and Osteryoung (*16*). The electrochemical polymerization of benzene in various ionic liquids to prepare poly(p-phenylene) has also been reported (*17-20*). In these studies, ionic liquids were used mainly as convenient electrolytes. Carlin and Osteryoung (*21*) produced a new electroactive material by electrochemical oxidation of triphenylsilyl chloride (Ph_3SiCl) in the acidic ionic liquid ($AlCl_3$-[emim]Cl). The film exhibited reversible redox behavior and was electronically conducting in oxidized state. They postulated that the cations of the ionic liquids took part in the formation of the film. However, one of the major drawbacks of chloroaluminate(III) based ionic liquids is that they are water-sensitive.

Very recently, Haddleton, et al. (*22*) used 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6), air and water-stable RTIL, as solvent for the Cu(I)-N-propyl-2-pyridylmethanimine mediated living radical polymerization of methyl methacrylate (MMA). They found that the rate of polymerization was enhanced as compared to other polar/coordinating solvents, even though the molecular weight of the resulted poly(methyl methacrylate) (PMMA) was low. Moreover, the polymer recovered was made essentially copper free by a simple solvent wash, which avoids the contamination of the polymer product by the catalyst.

In this study, we set out to evaluate the potential utility of neutral, air stable RTILs for conventional free radical polymerization of styrene, MMA, and acrylic acid (AA) in [bmim]PF_6 and/or [hmim]PF_6 (hmim = 1-hexyl-3-methylimidazolium cation). Benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) were used as radical initiators. The isolation, purification, molecular weights, and microstructures (tacticity) of the polymers were investigated, along with the potential of RTILs for use in block copolymer formation using conventional free radical initiators.

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Experimental

Materials

Styrene (Aldrich, 99%), MMA (Aldrich, 99%), and AA (Aldrich, 99%) were distilled to remove inhibitors and stored in calibrated ampoules. [bmim]PF_6 and [hmim]PF_6 (provided by Sachem Inc. or synthesized as reported elsewhere (*12*)) were washed with pure water five times. Benzene (Fisher, ≥ 99%) and toluene (Fisher, ≥ 99.8%) were distilled from freshly crushed calcium hydride. BPO (Aldrich, 97%) and AIBN (Aldrich, 98%) were recrystallized from methanol.

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Instrumentation

Size exclusion chromatography (SEC) was used to measure molecular weights and molecular weight distributions, M_w/M_n, of organo-soluble polymer samples with respect to PMMA or polystyrene (PS) standards (Pressure Chemical Co.). The SEC experiments were carried out at 30 °C in THF using a Waters 510 pump and Waters 410 differential refractometer detector (flow rate: 1 mL/min, columns: Waters 500 Å, 10^3 Å, 10^4 Å, 10^5 Å, 10^6 Å). Aqueous SEC with pullulan standards (pullulan is a water soluble polysaccharide commonly used as a calibrant in aqueous SEC) was used to estimate molecular weights of poly(acrylic acid) specimens.

^1H and ^{13}C NMR spectra of the polymers were obtained using a Bruker ARX-400 spectrometer at room temperature. Sample concentrations were between ca. 10-25% (w/v) in $CDCl_3$. Trace $CHCl_3$ in $CDCl_3$ (7.26 ppm for ^1H and 77.3 ppm for ^{13}C) or TMS (0 ppm) was used as an internal reference.

Polymerization

All polymerizations were performed under high vacuum to ensure that the systems were oxygen free. After charging the initiator (BPO or AIBN) and solvent ([bmim]PF_6 or [hmim]PF_6) into a round bottom flask with a constriction, the system was degassed for 2 h and a pre-determined quantity of monomer (styrene, MMA, or AA) was distilled into the reactor. The flask was removed from the vacuum line by heat sealing at the constriction and placed in a pre-heated water bath (65 °C for AIBN and 75 °C for BPO). The polymerization was allowed to continue for about 4~8 h and then stopped by precipitation into methanol ([bmim]PF_6 is soluble in methanol). In the case of copolymerization, the first block was made by the same procedure described above, using a shorter polymerization time (< 4 h). After taking about 5 mL of solution for sampling, the unreacted monomer was pumped away. Then a pre-determined quantity of the second monomer (such as MMA) was distilled in the system, and the reaction was kept at a lower temperature (room temperature) for a longer time (e.g., up to 4 days). The MMA and styrene polymers were isolated gravimetrically, methanol was used to remove residual RTIL, and the pure polymers were dried under vacuum. In the case of poly(acrylic acid), the polymer was extracted from the RTIL using water.

Results and Discussion

Homopolymerization in [bmim]PF_6 or [hmim]PF_6

Table I shows results from homopolymerization of MMA and AA initiated by AIBN in [bmim]PF_6 or [hmim]PF_6. From the Table we can see that PMMA obtained using AIBN in [bmim]PF_6 or [hmim]PF_6 have very high molecular weights, much higher than for PMMA made using a conventional VOC solvent, e.g., benzene, at the same monomer to initiator ratio. The polymers exhibit typical polydispersities for free radical polymerization products, despite the fact that the polymers are insoluble in the reaction medium. Also, we noted that the polymerizations were rapid; complete conversion of monomer to polymer was achieved after eight hours polymerization time. Thus, it seems that the viscous nature of the RTIL solvent, plus the precipitation of the polymeric radicals as the polymerization proceeds leads to "diffusion controlled termination" throughout the polymerization. A diminished rate of termination would explain both the higher than expected molecular weights and rapid polymerization rates. For the polymerization of AA initiated by AIBN in [hmim]PF_6, the polymer remained soluble and polydispersities were very broad. That is not surprising for radical polymerization of AA (*23*).

Figure 1 shows the SEC traces of polystyrene (PS) obtained from BPO in [bmim]PF_6 and benzene. Even though the reaction conditions were almost the same, the molecular weight of PS obtained from BPO in [bmim]PF_6 is much higher than that obtained from BPO in benzene. This confirms the prior observations regarding molecular weights of PMMAs made in RTILs that are nonsolvents for PMMA. As above, we explain the higher molecular weights by the fact that [bmim]PF_6 is a nonsolvent for PS, and as the polymerization proceeds PS chains form a monomer swollen polymer phase limiting polymer termination (radicals in this entangled polymer phase have difficulty diffusing

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Table I. Homopolymerization of MMA and AA in RTIL

Synthesis of PMMA in [bmim]PF$_6$^{a}

Run	IL (mL)	MMA (mL)	AIBN (mmol) x 10^{-3}	Temp. °C	M_w x 10^{-5}	M_n x 10^{-5}	M_w/M_n
1	9	1	6.1	70	7.61	3.71	2.05
2	9	1	30.4	70	6.94	3.40	2.04
3	9	1	183.1	70	5.03	2.44	2.06

Synthesis of PMMA in [hmim]PF$_6$

Run	IL (mL)	MMA (mL)	AIBN (mmol) x 10^{-3}	Temp. °C	M_w x 10^{-5}	M_n x 10^{-5}	M_w/M_n
1	1.8	0.2	36.5	70	2.99	1.85	1.62
2	1.8	0.2	183.1	70	1.06	0.60	1.77

Synthesis of PAA in [hmim]PF$_6$

Run	IL (mL)	AA (mL)	AIBN (mmol) x 10^{-3}	Temp. °C	M_w x 10^{-5}	M_n x 10^{-5}	M_w/M_n
1	1.8	0.2	36.5	65	2.10	0.38	5.53
2	1.8	0.2	183.1	65	2.23	0.44	5.07
3	1.8	0.2	365.3	65	2.00	0.34	5.88

[a] Polymerization of MMA in benzene (AIBN, 65 °C): $M_n = 91.3$ K, $M_w/M_n = 1.84$.

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together). The polymer can be gravimetrically separated from the reaction mixture in such instances, making polymer isolation easy.

The unique characteristics of RTILs may also offer new possibilities to tailor polymer properties. Thus, we investigated the tacticity of PS and PMMA obtained using [bmim]PF$_6$. Figure 2 shows the ^{13}C-NMR spectra of carbonyl regions in PMMA obtained from various polymerization mechanisms. It is well known that the chemical shifts of carbonyl groups in PMMA are very sensitive to tacticity (22). Our preliminary data suggest that the tacticity of PMMA prepared by radical polymerization in RTILs is essentially equivalent to that produced using conventional radical polymerization, as indicated in Figure 2. Detailed studies of the microstuctures of PMMA obtained from various RTILs and the microstructures of other methacrylate and acrylate derivatives are in progress.

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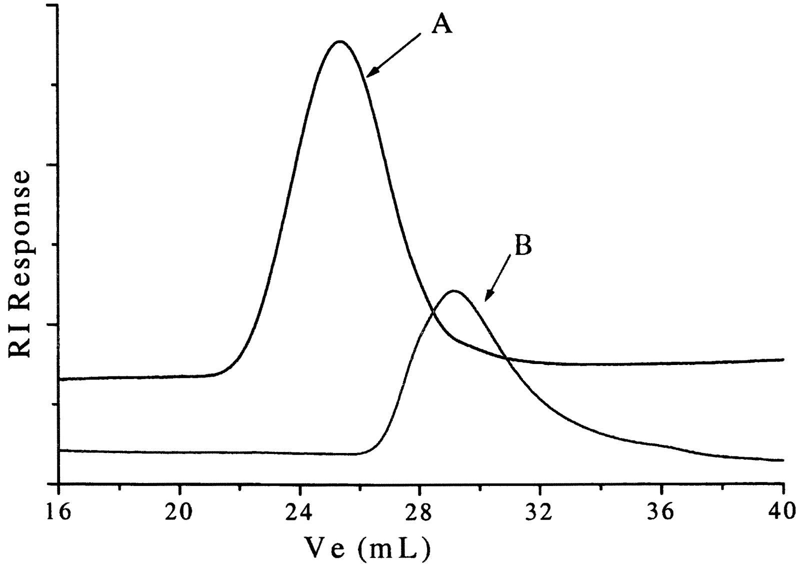

Figure 1. *SEC Traces of PS (A) from styrene (1.5 mL) polymerized by BPO (5 mg) in [bmim]PF_6 (15 mL) at 75 °C for 8 h, Mp ~800 kg/mol, M_w/M_n ~2.2; (B) from styrene (6.2 mL) polymerized by BPO (20 mg) in benzene (40 mL) at 75 °C for 15 h; Mp ~231 kg/mol, M_w/M_n ~2.5.*

Copolymerization of Styrene and MMA in [bmim]PF_6

The poor solubilities of most polymers in RTILs, and the resulting apparent diffusion limited termination behavior, stimulated us to attempt to make block copolymers using conventional free radical polymerization with sequential addition of monomers. Figure 3 illustrates the SEC traces for the block copolymerization of styrene and MMA (styrene was polymerized first). Although there is PS homopolymer present in the unfractionated diblock, the polymer is mostly diblock (refractive index increment, dn/dc, for PMMA is much smaller than dn/dc for PMMA in THF (about 0.19 versus 0.11 mL/g, respectively), meaning that the amount of PS homopolymer in chromatogram B is much less than it appears). After extraction using cyclohexane to remove the

PS homopolymer, NMR was used to confirm the copolymer nature of the purified diblock (chromatogram C). It should be noted that negligible PMMA homopolymer formation occurs because the solution was never exposed to temperatures higher than room temperature after addition of MMA. The rate of decomposition of BPO to generate free radicals is essentially zero at such low temperatures.

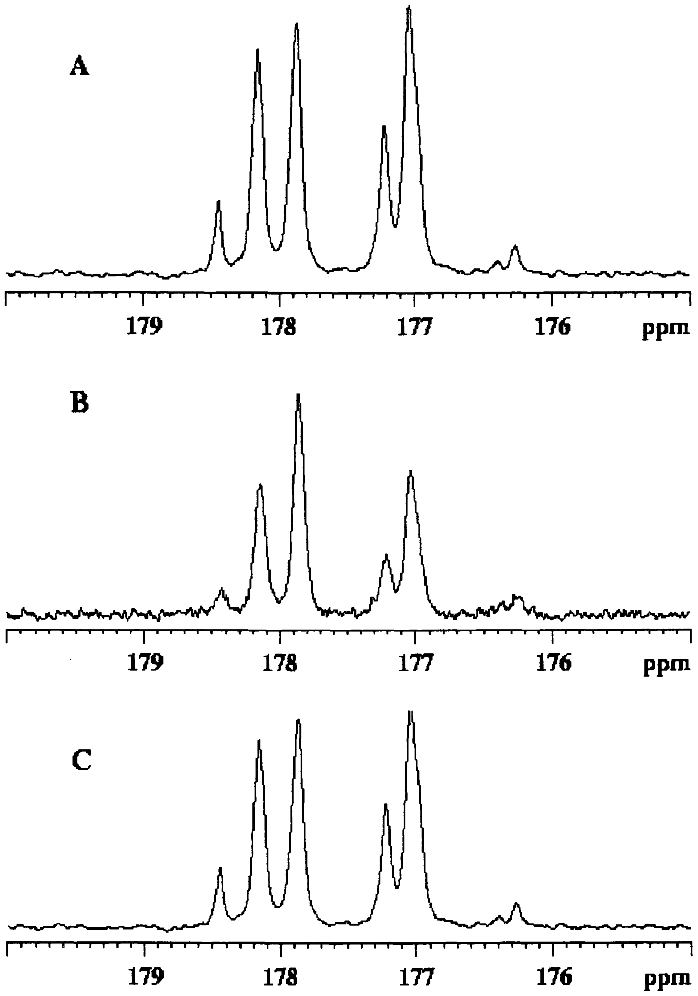

Figure 2. *^{13}C NMR spectra of PMMA (carbonyl regions) (A) from AIBN in [bmim]PF_6; (B) from BPO in [bmim]PF_6; (C) from BPO in benzene.*

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The success of this process depends on the precipitation of the first block, which will trap some of the propagating centers (radicals) and keep them "living" (by minimizing coupling and/or disproportionation). When the second monomer is added, it diffuses to the radical sites, polymerization continues, and block copolymer is formed. The appropriate choice of reaction temperatures and reaction times during polymerization of the two blocks is also very important. Typically, one should utilize higher temperatures and shorter times for polymerization of the first block relative to the second block. The higher temperature during formation of the first block, promotes relatively rapid radical formation with initiators like BPO and AIBN. The use of a much lower temperature during polymerization of the second monomer minimizes generation of new free radicals that would lead to homopolymer contaminants derived from homopolymerization of the second monomer by newly created radicals. Though rigorous characterization of the final products is still in progress, the preliminary results presented herein clearly demonstrate that it is possible to make block copolymers in RTILs by simple sequential addition of monomers.

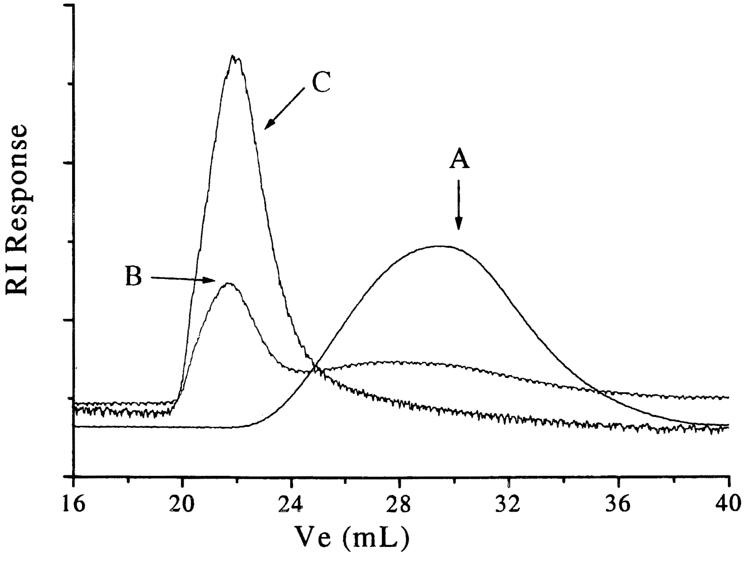

Figure 3. SEC Traces of (A) PS block from BPO in [bmim]PF$_6$, (B) PS-b-PMMA after adding MMA to PS block (before extraction), (C) PS-b-PMMA after extracting with cyclohexane.

Conclusions

The room temperature ionic liquids [bmim]PF_6 and [hmim]PF_6 were used as solvents for conventional free radical homopolymerization of styrene, MMA, and AA. For PMMA and PS chain growth, the degree of polymerization obtained using ionic liquids was much higher than that obtained via conventional radical polymerization in benzene using the same monomer and initiator charges. Rates of polymerization were also rapid for these systems, relative to polymerization in common organic solvents. We believe that the simultaneous rapid polymerization rates and high molecular weights are due to diffusion-controlled termination, reflecting both the high viscosity of the RTILs and phase separation. The polymers were also easily (gravimetrically) isolated from the reaction medium because of the insolubility of PS and PMMA in [bmim]PF_6 and [hmim]PF_6. Residual RTIL could be removed with alcohol, making this polymerization process potentially attractive for "Green" polymer synthesis. There were no major differences in tacticity of PMMA made in RTILs as compared to PMMA obtained from conventional solution radical polymerization.

Sequential monomer addition under the appropriate conditions of temperature and reaction time allowed synthesis of block copolymer in high yield using conventional free radical initiators and RTILs as solvent. This method shows great promise for economical and 'green' synthesis of a wide range of block copolymers.

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Chapter 10

Effect of Room-Temperature Ionic Liquids as Replacements for Volatile Organic Solvents in Free-Radical Polymerization

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Room temperature ionic liquids (RTILs) are a class of solvents that can be used in polymer synthesis to replace volatile organic compounds. However, to make the transition of ionic liquids from laboratory scale to industrial scale, the reactions must be feasible, they must produce polymers that have similar or better mechanical properties to traditional methods, and the ionic liquids must be recyclable. Polystyrene, poly(methyl methacrylate), and poly(2-hydroxyethyl methacrylate) were made by bulk and solution polymerization using both traditional organic solvents and ionic liquids. The monomer and polymer solubilities were tested in the ionic liquids, and physical properties, including the tensile moduli and glass transition temperatures, were measured. Results are encouraging, in that the tensile moduli are not statistically different whether the polymer was formed in organic solvent or in ionic liquid solvent.

Background

Our society today is inundated with plastics. Products ranging from drink bottles, to computer casings, and even medical supplies are made from plastic. In fact, it has been estimated that over 80 billion pounds of plastics are produced annually in the United States alone (1). The majority of these plastics are made via free radical addition polymerizations and over half of these are solution polymerizations (2).

Most solution polymerization reactors utilize volatile organic compounds (VOCs) as solvents, which are well known to be environmental and health hazards. Environmental hazards include smog and air pollution, while health hazards include eye, skin, and central nervous system irritation.

VOC usage in chemical manufacturing industries is rampant, with over five billion dollars worth used annually worldwide (3). An example of this widespread usage is in polystyrene production, one of the most widely made commodity polymers. In 1999, the domestic production of polystyrene was 6.5 billion pounds (1). Almost all of the polystyrene produced commercially uses ethylbenzene, a VOC, as a solvent. It has been suggested by one source that for every ton of polystyrene produced, over 2.5 pounds of VOC emission occurs, suggesting that over 4,000 tons of volatile organic compounds are released into the atmosphere yearly from the US production of polystyrene alone (5).

Clearly, major environmental problems could be on the horizon if these large quantities of VOCs continue to be used and released. For this reason, new, environmentally sound manufacturing processes are being investigated. One of the possibilities is solvent-free reaction conditions, but this is not always feasible, especially in polymerizations, where the judicial selection of a solvent can improve reaction conversion significantly. This leads to the investigation of new solvents that can be used successfully in reactions, but have a smaller impact on the environment. Some of the solvents now being studied as replacements to VOCs include water, supercritical fluids such as carbon dioxide, and ionic liquids (6-8).

We believe ionic liquids are one of the most promising of these new alternate solvents and have focused our research efforts on determining the feasibility of using ionic liquids as solvents for free radical addition polymerizations. To effectively replace VOCs with RTILs, there are several issues that must be addressed: solubility, solvent recovery and recycling, polymerization kinetics, and the structural and mechanical properties of the polymers produced.

Due to the unique nature of ionic liquids and the relatively recent revitalization of interest in these substances, there has been little research reported on polymerization in ionic liquids. Of the articles published, the research on polymerizations using ionic liquids has been more concerned with catalyst development rather than studying mechanisms of polymer kinetics or the structures formed. In 1990, Carlin and Wilkes studied the polymerization of ethylene in a chloroaluminate ionic liquid, $AlCl_3$-1-ethyl-3-methylimidazolium chloride using Ziegler-Natta catalysts (9). In 1992, Kobryanskii and Arnautov

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observed the electrochemical polymerization of benzene in an aluminum chloride and *N*-butylpyridine chloride based ionic liquid (10) and in 1993 they used the same solvent for an oxidative polymerization (11). In 1994, Goldenberg and Osteryoung (12) also synthesized polyphenylene by electropolymerization in 1-ethyl-3-methylimidazolium ionic liquid. Since these investigations, there have been no reports of subsequent research, or any record of polymerizations in non-chloroaluminate ionic liquids outside of the recent work of the groups of Mays and Haddleton, included in this monograph.

Ionic liquids have several characteristics that make them excellent candidates for use as solvents in polymerizations. They are highly solvating and have been shown to dissolve both organic and inorganic compounds. They are highly thermally stable, which is extremely important due to the exothermic nature of most free radical polymerization reactions. Ionic liquids also are believed to support long free radical lifetimes(13), suggesting higher conversions would be obtained in polymerizations carried out in ionic liquids versus those carried out in VOCs.

From an environmental point of view, there are also many reasons ionic liquids are preferred over VOCs. First and foremost is that they are nonvolatile and nonflammable, eliminating two of the primary environmental concerns with VOCs. Secondly, by eliminating the use of VOCs, the costly and potentially hazardous transportation and disposal of VOCs trapped by effluent scrubbers would become unnecessary. A third advantage of ionic liquids is that they are recyclable, which results in significantly less waste generated by polymer production.

Free radical polymerizations follow a three-step mechanism (initiation, propagation, and termination) to rapidly produce high molecular weight polymers. Solution polymerization provides several advantages for these reactions, as the solvent can help to:

- overcome diffusion limitations by creating a more fluent environment which leads to higher conversion and higher polymer molecular weight,
- control viscosity allowing easier mixing, and
- dissipate heat in the reactor by absorbing heat released during the polymerization reaction.

There are disadvantages to consider with solution polymerizations as well, including:

- contamination of the polymer by residual solvent, and
- reduction in conversion due to chain transfer.

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When VOCs are used, residual solvent can be removed by evaporation, but this is not possible with RTILs since they are nonvolatile. An ideal way to remove polymer from solvent would be simple decantation if the polymer and solvent were insoluble. Other possible means of separation include using supercritical carbon dioxide, diethyl ether, or using a water soluble RTIL and extracting it (with water) after the reaction is complete. Chain transfer may also impact polymerization when using a solvent, as the solvent itself may absorb free radicals, resulting in polymers with lower average molecular weights and inferior physical properties. Chain transfer is dependent on the solvent, monomer, and initiator being used (2):

$$\frac{1}{\overline{X}_n} = \frac{R_i}{2R_p} + C_m + C_s\frac{[S]}{[M]} + C_i\frac{[I]}{[M]} \tag{1}$$

where X_n is the number average degree of polymerization, R_i is the rate of initiation, R_p is the rate of propagation, C values represent chain transfer coefficients for monomer, solvent and initiator, and [M], [S] and [I] are concentrations of each species in the polymerization solution. As can be seen in equation (1), chain transfer affects the chain length, with the solvent (due to its relatively high concentration) often being the main barrier to reaching high molecular weights.

Experimental

Three polymer systems were selected, as shown in Table I. Polystyrene, PS, and

Table I. Polymerization Systems Studied

Monomer	*Cross Linking Agent*	*Solvent*
styrene	divinyl benzene	[a] bmim$^+$ PF_6^-
styrene	divinyl benzene	ethyl benzene
MMA	[b] EGDMA	[a] bmim$^+$ PF_6^-
MMA	[b] EGDMA	methanol
HEMA	[b] EGDMA	[c] bmim$^+$ Cl^-
HEMA	[b] EGDMA	ethanol

[a] 1-butyl-3-methylimidazolium hexafluorophosphate
[b] ethylene glycol dimethacrylate
[c] 1-butyl-3-methylimidazolium chloride

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poly(methyl methacrylate), PMMA, were chosen because they are two of the most widely-used commodity polymers, and as such their synthesis and properties have been well documented. Poly(2-hydroxyethyl methacrylate), PHEMA, was also selected because it is a material used in manufacturing biomaterials such as contact lenses, and being hydrophilic has markedly different solubility characteristics from PS and PMMA. The solubilities of monomers and polymers were tested with the solvents at 55 °C at 50 vol % monomer, except for styrene, which was tested at 40 vol % monomer. Table II shows the solubilities of the PS, PMMA and PHEMA in the RTILs tested.

Table II. Monomer and Polymer Solubilities in Ionic Liquids

Species	*bmim⁺ PF₆⁻*	*bmim⁺ Cl⁻*
styrene	+	-
MMA	+	-
HEMA	+	+
AIBN	+	+
PS	-	-
PMMA	-	-
PHEMA	-	+

Note: (-) indicates that two separate liquid phases were present at the conditions tested. (+) indicates that the material was completely soluble at the experimental conditions, although upper solubility limits have not been established.

Crosslinked PHEMA and PMMA were formed by free radical solution polymerization using 50 vol % of either a VOC or an ionic liquid and one mole percent crosslinking agent. The solution was purged with nitrogen to displace any dissolved oxygen, a free radical scavenger. One weight percent 2,2'-azobisisobutyronitrile (AIBN), a thermal initiator, was added to the solution, which was then injected between two glass plates to ensure uniform sample thickness. The reactions were carried out at 55 °C for twenty hours to ensure the reaction had gone to completion.

Polymer samples were removed from glass plates and cut into samples of uniform size. Because the ionic liquids were trapped in the polymer mesh, a separation technique was needed to recover the polymer. Solvent extraction was accomplished through rinsing the PMMA samples in an 80% ethanol/ 20% water solution and the PHEMA samples in water, each for four days. After rinsing, the samples were dried in a vacuum oven at 40 °C to constant weight. Upon drying, various physical properties of the samples were tested.

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To ensure that polymers formed in ionic liquids have mechanical properties that are either comparable or superior to those formed in traditional solvents, the tensile moduli and the glass transition temperatures of the polymers were determined experimentally. The tensile modulus, G, is a measure of the ability of a polymer to resist deformation when subjected to stress. A high tensile modulus is desirable in polymers that will be used as structural materials. This is important when considering the commercial applicability of polymers formed with ionic liquids, which must be as resilient as those formed with VOCs. The tensile modulus was measured with an Instron automated materials testing apparatus (Model 4465, Canton, MA). The samples were stretched by applying a strain in the axial direction while measuring the force required to maintain a constant 10 mm/min strain rate. The stress-strain data were essentially the same for PHEMA samples formed in bmim$^+$ Cl$^-$ and ethanol, as long as the solvent was extracted after polymerization (note the identical curves in Figure 1). If the RTIL remained in the polymeric structure, the mechanical behavior of the polymer was compromised significantly, as the stresses decreased by three orders of magnitude for PHEMA with 50 vol % bmim$^+$ Cl$^-$ remaining inside the network.

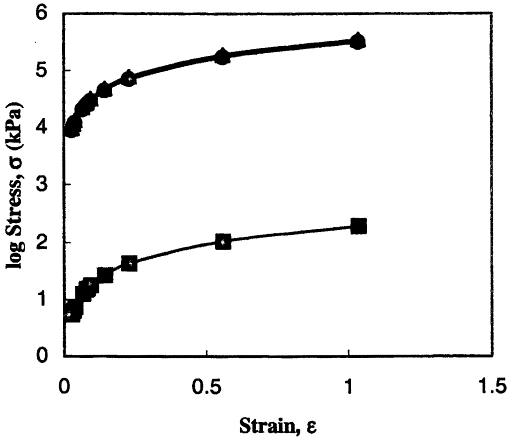

Figure 1. Stress-strain diagram for PHEMA samples with a constant strain rate of 10mm/min. (■) represents PHEMA containing unextracted bmim$^+$ Cl$^-$ (▲) represents PHEMA made in bmim$^+$ Cl$^-$, after the solvent is extracted, and (●) represents PHEMA made in ethanol, after extraction of the ethanol.

Another important measure of a polymer's integrity is the glass transition temperature (T_g). At temperatures above T_g the amorphous regions have translational and rotational energy, allowing the chains to rotate, creating a polymer that is pliable and soft. For ionic liquids to have viable industrial applications the T_g of polymers formed should be the same or higher as those produced using VOCs.

The glass transition temperatures of the samples were measured with a differential scanning calorimeter, DSC (TA Instruments, Model 2960, New Castle, DE). The samples were heated from ambient temperature across the T_g at a ramp rate of 10 °C/min. The glass transitions were determined by the change in heat capacity as the temperature is ramped, denoted by the inflection point in Figure 2.

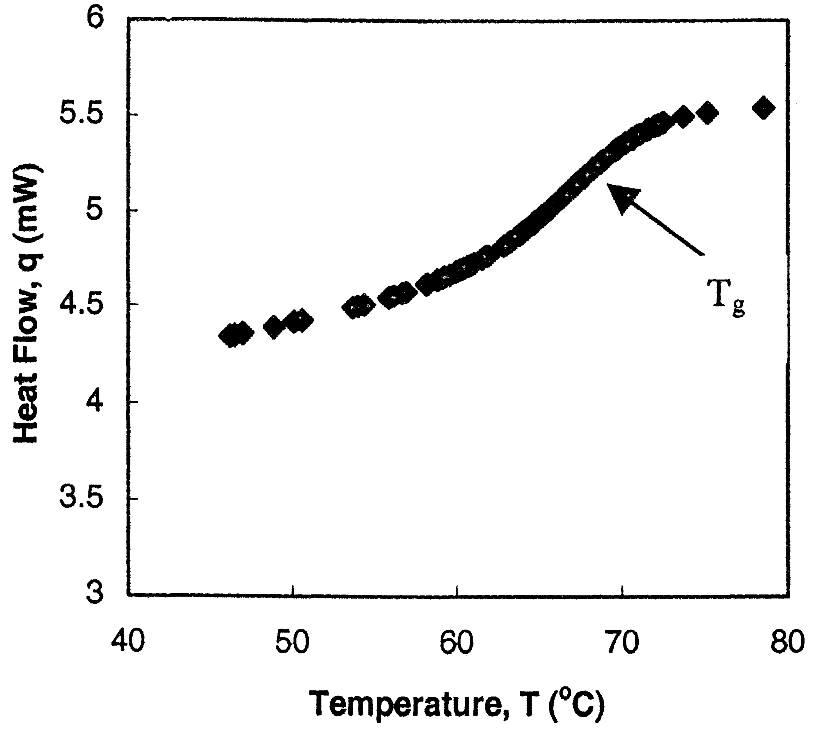

Figure 2. Differential scanning calorimetry thermogram of a bulk PMMA sample. The glass transition temperature is marked at the center of the slope change.

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Results/Discussion

The tensile moduli and glass transition temperatures were measured for various samples of PMMA and PHEMA (the testing of polystyrene is ongoing). In addition to using a VOC solvent and an ionic liquid solvent, samples made without a solvent (bulk polymerizations) were also tested (Table III).

Table III. Glass Transitions and Tensile Moduli of Polymers formed by Bulk and Solution Polymerizations

Polymer	*Solvent*	*Extracted?*	*Glass Transition, T_g (°C)*	*Tensile Modulus, G (MPa)*
PMMA	none (bulk)	N/A	65	525
PMMA	bmim$^+$ PF$_6^-$	no	<23	0.630
PMMA	bmim$^+$ PF$_6^-$	yes	80	579
PMMA	methanol	yes	92	549
PHEMA	none (bulk)	N/A	75	
PHEMA	bmim$^+$ Cl$^-$	no	<23	0.192
PHEMA	bmim$^+$ Cl$^-$	yes	86	310
PHEMA	ethanol	yes	87	342

Note: Tensile modulus data represent the average of two to three experiments.

The results shown indicate that ionic liquids can be used as solvents for free radical polymerizations without significantly changing the physical properties of polymers. In addition, the physical integrity of the polymers were maintained after the solvent change. The glass transition temperatures for PHEMA and PMMA produced in ionic liquid solvents were very similar to those produced in VOCs. The tensile moduli of polymers formed in ionic liquids were statistically equal to those of polymers produced in VOCs. In the case of PMMA the value obtained using the ionic liquid was actually higher than was achieved using a VOC or bulk process, supporting the suggestion that free radical lifetimes are longer in ionic liquids than VOCs. Based on this observation, ionic liquid solvents may be used in the future to develop even stronger PMMA polymers than exist today.

While the development of ionic liquids for use in manufacturing processes is still in its early stages, it is clearly within the realm of possibility that many commodity polymers could one day be made with ionic liquid solvents, rather than VOCs. This would result in a tremendous reduction in pollution caused by the volatility and disposal problems associated with traditional solvents. In order for widespread industrial VOC replacement to become a reality, it is necessary to better understand the kinetics of polymerization, solubility and compatibility of many more monomers with RTILs, and to simplify the separation step so the ionic liquid can easily be recycled.

Acknowledgments

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Chapter 11

Green Synthesis: Aromatic Nitrations in Room-Temperature Ionic Liquids

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As one of the least environmentally compatible synthetic methods, aromatic nitration has attracted a great deal of effort in terms of the design of more benign techniques. Room temperature ionic liquids (RTILs) afford a useful new method for aromatic nitration by using a simple nitrating agent (nitric acid) with a transition metal catalyst. Distillation of the nitration products affords a solvent/catalyst system that can be readily recycled for at least 4 reactions.

Introduction

Electrophilic aromatic substitution chemistry is of critical importance in a wide variety of industrial, fine chemical, and academic processes (*1*). While this chemistry is well developed and performed on the metric ton scale, it is also a prime example of how "black" synthesis can be. The majority of these aromatic substitution processes involve large amounts of moisture sensitive and toxic reagents and produce even greater quantities of highly acidic and/or

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

water-reactive wastes. For example, most Friedel-Crafts acylation reactions involve the suprastoichiometric use of aluminum trichloride. (Figure 1) Upon work-up, this results in the formation of large amounts of highly acidic aqueous waste from the hydrolysis of the aluminum "catalyst." Although this is the most cited example of the environmentally damaging aspects of electrophilic aromatic substitution chemistry, aromatic nitrations are no better. Aromatic nitration is typically catalyzed by the use of concentrated sulfuric acid in conjunction with concentrated nitric acid. (Figure 1) Again, upon work-up this leaves an acidic aqueous waste layer that must be disposed.

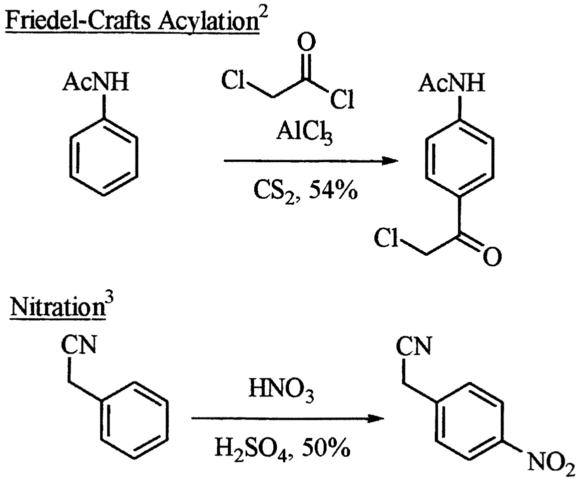

Figure 1. Electrophilic Aromatic Substitution Reactions

Alternative Methods of Aromatic Nitration

Given the problems associated with aromatic nitration reactions and the tremendous demand for materials of this type, considerable effort has been directed toward making this chemistry more environmentally compatible. While a number of alternatives to the use of sulfuric acid as the catalyst for aromatic nitrations have been developed (most notably various acidic zeolites (*4*), metal-exchanged clays (*5*), or super-acidic polymers (*6*)), virtually all of these reaction conditions require either the use of exotic nitrating agents (particularly N_2O_4 or nitronium salts) or the addition of acetic anhydride (for *in*

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situ formation of the acyl nitrate). (Figure 2) Further, many of these reaction conditions are "solvent-free" - that is, the aromatic substrate serves as the solvent for the reaction. This is an ideal situation for bulk industrial nitrations of simple, inexpensive aromatics such as benzene or toluene. In the case of fine chemical or academic scale synthesis, "solvent free" conditions are not as practical. Many more functionalized aromatic compounds are not liquids, which necessitates the use of a reaction solvent. Further, complete separation of the nitration product from the solid acid catalyst generally requires some type of extraction, which reintroduces the problems associated with a volatile organic solvent.

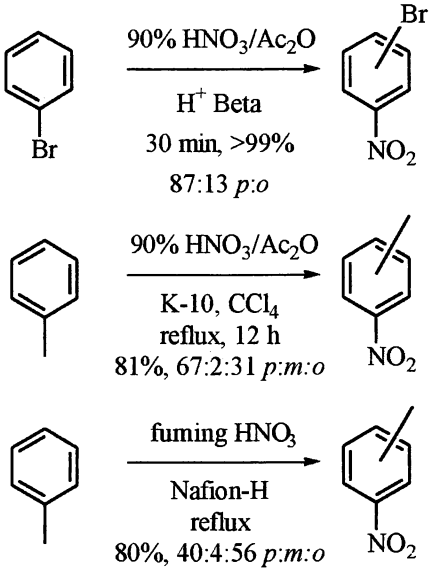

Figure 2. Alternative Nitration Methods

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Nitrations with Nitric Acid

From either an industrial or environmental standpoint, the ideal nitration agent is commercial grade 70% aqueous nitric acid, which is inexpensive and generates water as the only waste product. To achieve this goal, a better method to activate nitric acid than the use of excess sulfuric acid is needed. A suitable method was reported a few years ago by Barrett and co-workers (*7*).

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(Figure 3) In their communication, they reported the use of ytterbium triflate as a catalyst for the nitration of aromatic substrates using stoichiometric 70% nitric acid as the nitrating agent. A number of substrates could be effectively nitrated, including modestly deactivated systems such as bromobenzene. Further, the catalyst could be recovered from the water layer following aqueous work-up. After drying, the resulting solid could be used to catalyze further nitrations. Two practical issues limit the application of this method. First, the catalyst must be separated and dried before it can be reused. In particular, the drying phase of this recycling is time and energy intensive. Second, the reaction solvent, dichloroethane, is an environmental and safety hazard. Both of these issues are precisely the types of situations where room temperature ionic liquids (RTILs) can play an important and successful role in enhancing the environmentally friendly nature of a process.

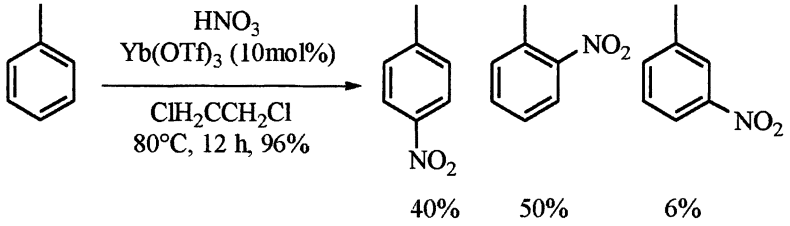

Figure 3. Aromatic Nitrations Using Nitric Acid

The Use of Room Temperature Ionic Liquids

Prior to discussing the research efforts using RTILs in aromatic nitrations, it is necessary to briefly review what RTILs are and how they can be beneficial (*8*). RTILs are exactly what their name implies: salts that are liquid at or below room temperature. While there are a considerable number of materials that have been reported as members of this family, the majority can be characterized as being a combination of a large organic cation with a weakly coordinating anion. (Figure 4) By far and away the most popular RTIL to date is 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM BF_4). This particular compound has been used as a solvent for a wide variety of organic reactions (*8*). More importantly, with this solvent there have been a number of examples of the ability to recycle both the solvent and a transition metal catalyst by simple extraction or decantation of the reaction product (*9*).

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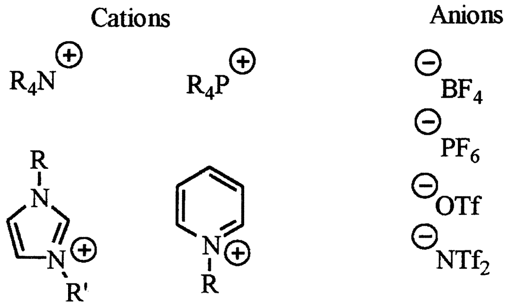

Figure 4. Major Classes of Room Temperature Ionic Liquids

Based on this precedent, it would appear reasonable to use BMIM BF_4 as a solvent for the aromatic nitration reaction. However, there is the possibility of nitrating the imidazolium ring as opposed to the aromatic reaction substrate. This is particularly a concern in the nitration of less electron rich (and hence less reactive) aromatic substrates. Indeed, during the course of our research, Laali and co-workers reported their study of the aromatic nitration reaction under a variety of conditions and in several RTILs (*10*). They did note that the imidazole ring of EMIM BF_4 was nitrated by nitrating agents such as nitronium tetrafluoroborate. Their optimal solution to this issue was the use of a combination of ammonium nitrate and trifluoroacetic anhydride as the nitrating agent and ethyldiisopropylammonium trifluoroacetate as the solvent. By employing these conditions, they were able to effectively nitrate a variety of aromatic substrates. For example, under these conditions, toluene afforded a 58% yield of a 54:4:42 mixture of the ortho, meta, and para isomers after 1 hour at room temperature (Figure 5).

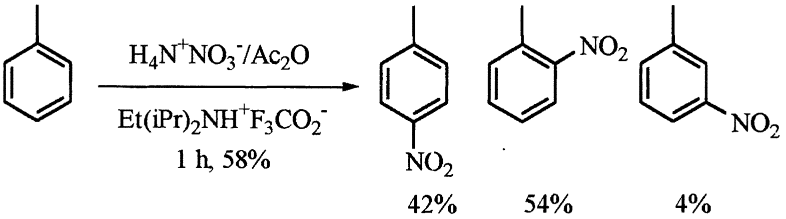

Figure 5. Laali's Nitration Conditions

Our efforts focused on the use of N-butyl, N-methylpyrrolidinium triflimide as the RTIL solvent (*11*). Both the cation and anion should be stable to the nitration conditions and thus could serve as a recyclable solvent system. As can be seen in Figure 6, the use of N-butyl, N-methylpyrrolidinium triflimide as the solvent with ytterbium triflate as the catalyst did afford the three nitrotoluene isomers in 95% yield. While the selectivity was not high, it was comparable to that observed under conventional conditions.

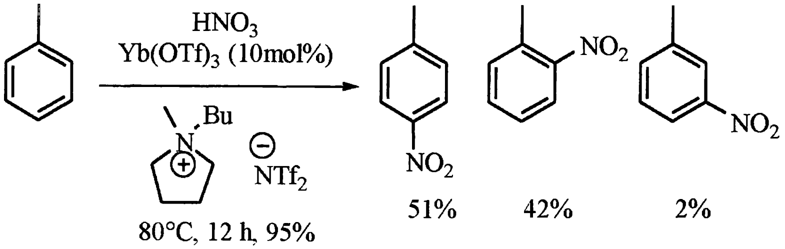

Figure 6. Aromatic Nitration of Toluene in a RTIL

Scope of Conditions

Using the same reaction conditions, a number of aromatic substrates were successfully nitrated. (Table I) Using substrates that were as or more electron-rich than benzene, good yields were obtained with regioselectivities typical of most nitration conditions. Importantly, anisole, a substrate that can undergo competitive oxidation in addition to nitration, afforded the desired nitration product in good yield (entry 2). However, substrates that were electron deficient, such as bromobenzene, did not undergo aromatic nitration under these conditions. In an effort to over come this limitation, the acyl nitrate was generated *in situ* using acetic anhydride or trifluoroacetic anhydride (*12*). With acetyl nitrate, very little reaction was observed (10% isolated yield of the product after 16 hours). However, by generating the trifluoroacetyl nitrate, bromonitrobenzene was isolated in 78% yield.

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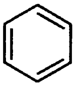
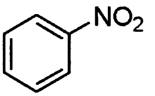
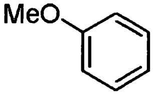
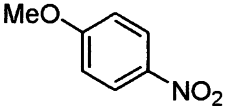
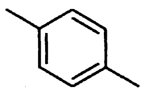
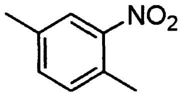
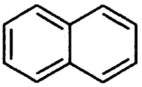
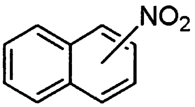
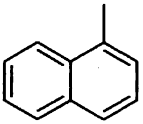
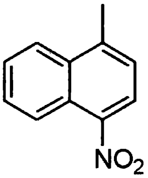
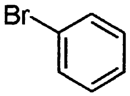
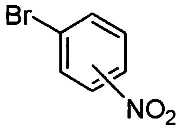
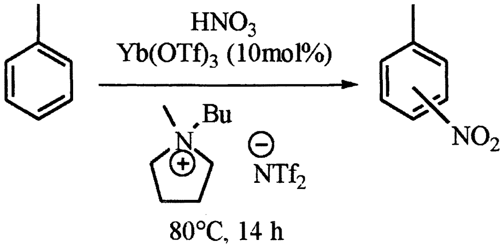
Table I. Ytterbium-Catalyzed Aromatic Nitrations[a]

Entry	*Substrate*	*Product*	*Yield*[b]	*Selectivity*[c]
1			97%	NA
2			78%	all *para*
3			93%	NA
4			86%	4 : 1[d]
5			57%	all 4-nitro
6			10%[e] 78%[f]	

a). All reactions performed on the 5 mmol scale using 1 equivalent of 70% aqueous nitric acid and 10 mol% of ytterbium triflate in 2 mL of ionic liquid at 80°C for 14-16 hours. b). Isolated yields. c). Determined by ^{1}H NMR. d). 1-nitro : 2-nitro ratio. e). Reaction performed with 1 equivalent of acetic anhydride. f). Reaction performed with 1 equivalent of trifluoroacetic anhydride.

Recycling

A major issue is the ability of the solvent and catalyst to be recycled. Using toluene as the test case, the RTIL and ytterbium catalyst could be recycled several times following separation of the nitrotoluene products. (Figure 7) It is important to note that, while the products can be separated by extraction, they can also be readily distilled out of the reaction solvent, thereby completely eliminating organic solvent waste. In our research, we have been accomplishing this by removing all volatile components by Kugelrohr distillation. This crude distillate is then dried with magnesium sulfate and filtered to remove the water by-product. The resulting product(s) is at least 90% pure by NMR. Using fractional distillation, even the need for drying agents could be obviated.



Run	Isolated Yield
1	95%
2	94%
3	95%
4	80%

Figure 7. Recycling Studies

Copper-catalyzed Nitrations

Despite this initial success, there is a practical issue to consider - the catalyst. Although using the RTIL conditions, both reaction solvent and catalyst can be recycled, the initial expense of using ytterbium triflate (roughly $10/g) is prohibitive on anything above an exploratory scale. One solution is to employ lower catalyst loadings to ameliorate this situation. A second alternative is to use a less expensive catalyst. A lead in this direction can be

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found in the area of water-tolerant Lewis acids. Lanthanide triflates have found considerable utility in this area, with scandium and ytterbium being the most active (*13*). However, copper triflate has been shown to have sufficient activity to catalyze many of these same reactions (e.g. Mannich and aldol condensations) in aqueous media (*14*). When coupled with the observation that copper and iron-exchanged clays are effective catalysts for aromatic nitration reactions (*15*), there is significant promise for this alternative. Additionally, copper triflate is less expensive ($3/g).

Results

Based on this hypothesis, copper(II) triflate was employed as the catalyst for the aromatic nitration of toluene. (Figure 8) Using the same solvent and conditions, the three isomeric nitrotoluene products were obtained in a near quantitative yield following Kugelrohr distillation from the reaction medium and drying with magnesium sulfate. Trace, colored impurities were removed by filtration through a plug of Celite to afford the nitrotoluene product in 93% yield. It is worth noting that the isomeric mixture differed only slightly from that obtained using ytterbium triflate as the catalyst.

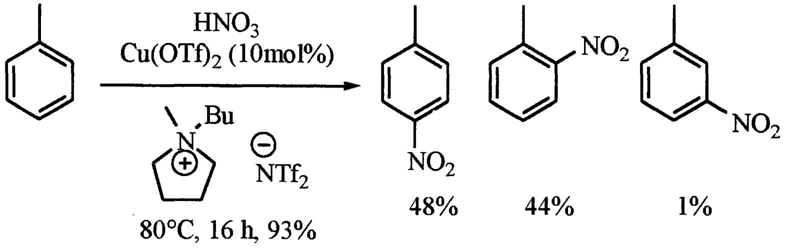

Figure 8. Copper-Catalyzed Reactions

Scope of Conditions

Employing these copper-catalyzed reaction conditions, a number of additional aromatic substrates were successfully nitrated. (Table II) As was the case with ytterbium triflate, substrates that were moderately electron-rich were nitrated in good yield, with regioselectivities typical of most nitration conditions (entries 1-3). With more electron-rich substrates, though, a major

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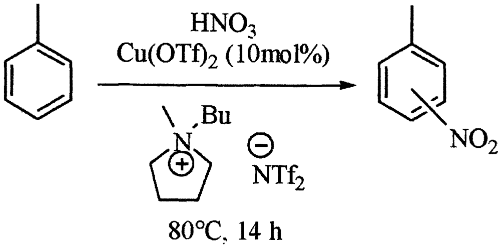
difference was noted (entries 2, 4, and 5). Addition of the nitric acid at room temperature to these electron rich substrates and copper(II) triflate resulted in an extremely exothermic reaction. After 2 hours, the nitration products could be isolated in good yield. This spontaneous reaction at room temperature was not noted with less electron rich substrates not was it noted with ytterbium triflate as the catalyst for any of the aromatic compounds. Finally, it should be noted that the regioselectivity of the nitration of the more electron rich substrates is reduced compared to the results obtained using ytterbium triflate.

Electron deficient substrates, such as bromobenzene, did not undergo aromatic nitration under these conditions, but nitration could be accomplished by generation of the acyl nitrate *in situ* using acetic anhydride or trifluoroacetic anhydride. As with the ytterbium triflate-catalyzed reactions, acetic anhydride afforded only modest conversion (15%). However, by generating the trifluoroacetyl nitrate *in situ*, bromonitrobenzene was isolated in 87% yield.

Recycling

As was the case with ytterbium triflate, the copper(II) triflate catalyst could be recycled after the reaction. Results from recycled catalyst/solvent were essentially the same regardless of whether distillative or extractive work-up conditions were employed. (Figure 9) Thus, on a small scale (1 mmol), extraction of the product with diethyl ether afforded the nitrotoluene isomers in



Run	Method of Separation	
	Extraction	Distillation
1	93%	94%
2	90%	92%
3	88%	

Figure 9. Recycling Studies

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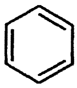
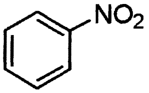
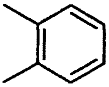
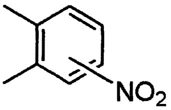
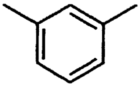
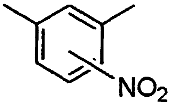
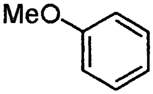
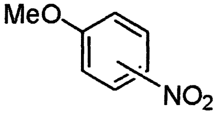
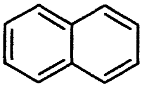
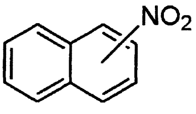
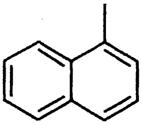
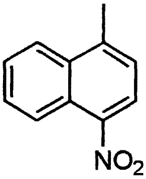
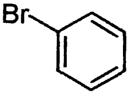
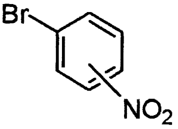
Table II. Copper-Catalyzed Aromatic Nitrations[a]

Entry	*Substrate*	*Product*	*Yield*[b]	*Selectivity*[c]
1			93%	NA
2			53%	2.4 : 1.0 (1,2,3:1,2,4)
3			90%	4.0 : 1.0 (1,2,4:1,2,3)
4[d]			80%	3.0 :1.0 (para:orthro)
5[d]			91%	3.5 :1.0 (1 : 2-nitro)
6[d]			96%	2.0 : 1.0 (4 : 2-nitro)
7			87%[e]	1.3 : 1.0 (para:ortho)

a). All reactions performed on the 2.5 mmol scale using 1 equivalent of 70% aqueous nitric acid and 10 mol% of copper(II) triflate in 2 mL of ionic liquid at 80°C for 14-16 hours. b). Isolated yields. c). Determined by ^{1}H NMR. d). Reaction performed at room temperature for 2 hours. e). Reaction performed with 1 equivalent of trifluoroacetic anhydride.

93, 90, and 88% yield over three runs, while on a larger scale (5 mmol), Kugelrohr distillation of the products afforded the same isomeric mixture in 94 and 92% yield over two runs. As such, it appears that either separatory method is compatible with recycling of the catalyst/solvent mixture.

Conclusion

In conclusion, we have developed a method for the nitration of aromatic compounds that utilizes 70% aqueous nitric acid as the nitrogen source and employs the less expensive copper(II) triflate in place of ytterbium triflate. In combination with RTILs, the catalyst can be recycled several times. Further, the reaction products can be removed by distillation, thus completely eliminating the need for conventional organic solvents. Efforts are underway to extend these reaction conditions to other types of aromatic substitution reactions, in particular Friedel-Crafts acylation and alkylation reactions.

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Chapter 12

Potential Application of Ionic Liquids for Olefin Oligomerization

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Olefin oligomerisation in ionic liquids provides exciting opportunities for the novel synthesis of industrially important compounds in a clean and more efficient way. Possibilities include the synthesis of base oils using α-olefins in acidic ionic liquids. In addition, preliminary investigations into chromium-catalysed trimerisation of ethylene and longer chain olefins in ionic liquids show promise. Some nickel-catalysed oligomerisation processes were already previously demonstrated to provide significant advantages when compared to homogeneous alternatives.

Ethylene, together with olefins from various hydrocarbon cracking or hydrocarbon forming processes, are the basic building blocks of the petrochemical industry. These easily available, cheap and reactive compounds are readily transformed by polymerisation and oligomerisation into a range of extremely versatile chemical intermediates that lead to a wide variety of industrial and consumer products, e.g. polymers and polyethylene comonomers, detergents, surfactants, synthetic lubricants (poly alpha olefins) and additives for lubricants, as well as plasticizers (*1*). Dimers and oligomers produced from α-

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

olefins can additionally be transformed into ethers or alkanes to produce high octane number additives for gasoline (*2*).

General Methods of Oligomerisation

In the past, oligomerisation was mainly achieved by using acidic catalysts. Mineral acids such as phosphoric or sulfuric acid can for instance be used for the oligomerisation of propene and butene (*3*), and branched C10 oligomers can be synthesised by employing a BF_3/BuOH catalyst complex (*1*). The use of these cationic oligomerisation methods is however limited, due to its poor selectivity and low activity towards linear olefins.

The use of highly electropositive metal organometallic catalysts for oligomerisation (e.g. Al), results in better selectivities and specificity. Relatively poor activities restrict their use however to specialised synthesis. Examples would be the one- and two step Ziegler processes (as developed by Albemarle and Gulf R&D Corp.), where triethylaluminium is employed to produce α-olefins from ethylene (*3*).

Coordination catalysts (consisting of a metal atom or ion, surrounded by a number of electron-pair donors called ligands) can be tailor-made by ligand variation. The catalyst complex is usually stable in more than one coordination number and, through fine-tuning of chemical bond strength (variation of the ligands), capable of holding a substrate molecule selectively but not too tightly (*4*). These catalysts therefore display diversified selectivities and a broader spectrum of activities (*5*). Homogeneous catalysis with these compounds often offer advantages such as milder conditions of pressure and temperature (when compared to heterogeneous systems), thus giving considerable advantages in specificity and selectivity. Important factors such as molecular weight, molecular weight distribution, as well as long- and short-chain branching can be controlled by careful catalyst design. A good example is the Shell Higher Olefin Process (SHOP) using a nickel catalyst in a polar phase such as 1,4-butanediol, to produce high purity α-olefins in a second phase (*3*). IFP's Dimersol process employs a Ziegler catalyst consisting of nickel compounds and aluminium trialkyls to dimerise propene and butene, in order to give predominantly branched olefins (*3*). Other examples include the use of metallocenes to produce very specific isomeric compounds with special properties (*6*), while well-chosen homogeneous chromium complexes trimerise ethylene to yield 1-hexene instead of a polymeric product (*7*).

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Biphasic Systems

Economic viability of homogeneous processes could be enhanced by catalyst recycling and recovery procedures. One of the most important developments of the last fifteen years in homogeneous catalysis is the introduction of biphasic techniques. In the case of biphasic catalysis it is assumed that the active catalytic specie is soluble in the solvent; reactants and reaction products are however not soluble, thus creating two phases. This concept combines the advantages of homogeneous catalysis (solvent effect, mild reaction conditions *etc.*) with those of heterogeneous catalysis (better use of the catalyst and easy product separation) (*8*). The nature of the solvent phase is of the utmost importance in catalyzed homogeneous reactions. An example would be coordinatively unsaturated cationic metal complexes (often the intermediate implicated in activation of organic molecules) which demand a solvent capable of stabilizing the cationic metal center. (*9*). The solvent-metal interaction should however be labile enough for displacement in order to allow for catalytic activity. The emergence of ionic liquids as possible alternative solvents for synthetic chemistry (originally applied only as electrolytes in the field of electrochemistry) opened a whole new field of chemistry. The diversity of ionic liquids available is huge, and although only a few different ionic liquids have been explored, they show the potential to be used as a very versatile tool for enhancing industrial chemistry.

Another very important motivation to consider ionic liquids as part of an industrial catalyst system, is the increasing pressure for the chemical industry to protect the environment and reduce pollution by using clean synthesis methods, which would imply for instance avoiding volatile organic solvents, especially chlorinated compounds. Ionic liquids are non-volatile compounds that display almost no vapour pressure, allowing for direct distillation techniques for almost any volatile product. In addition, they create the opportunity for biphasic catalysis whereby homogeneous catalyst systems can easily be recovered and recycled.

Ionic Liquids as Oligomerisation Catalyst

The acid-base properties exhibited by chloroaluminate ionic liquids (*10*) are well known. Acid chloroaluminate ionic liquids could therefore themselves act as catalysts, and should have the potential to be effective olefin oligomerisation catalysts. The oligomeric products would have very low solubility in the ionic liquid, and should separate as a less dense second phase to be easily removed by

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phase separation. Secondary reactions like isomerisation of the product could further be minimised by the immediate and complete separation between product and catalyst. This concept was illustrated by BP, where a mixed butene raffinate stream was oligomerised using an acidic chloroaluminate ionic liquid (*11, 12*). These oligomers can be used to react with alkenyl succinimides, which are useful fuel and lubricating oil additives. BP claimed in a subsequent patent that it should also be possible to oligomerise higher carbon chain length olefins using acid chloroaluminate ionic liquids, and that these products could be applied as synthetic lubricants (*13*).

Oligomerisation investigations using 1-decene with chloroaluminate ionic liquids as catalyst showed very low activity when ionic liquids with low acidity were used (e.g. [bmim]Cl-$AlCl_3$; [$AlCl_3$] ≤ 52%). Higher acid value ionic liquids easily oligomerised 1-decene, resulting in highly isomerised, high molecular weight oligomers. Control on the oligomer distribution proved to be difficult; some control could be obtained by changing the ionic liquid acidity, alkyl chain length on the cation, catalyst concentration, reaction temperature and solvent added, but a large amount of heavy oligomers ($> C_{40}$) were present in most of the samples.

In order to illustrate the amount of isomerisation taking place when different catalyst technologies are employed for olefin oligomerisation, gas chromatograms (GC) of the C10 oligomer distribution (*14*) using the following technologies are shown: i) the above-described acid ionic liquid catalyst (Figure 1); ii) commercial BF_3/BuOH catalyst technology (Figure 2); and iii) metallocene catalyst technology (Figure 3):

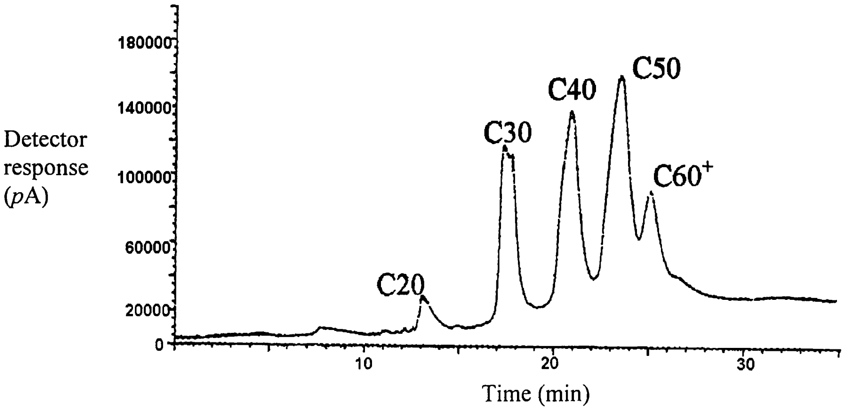

Figure 1. Polyalphaolefin obtained by employing an acid ionic liquid.

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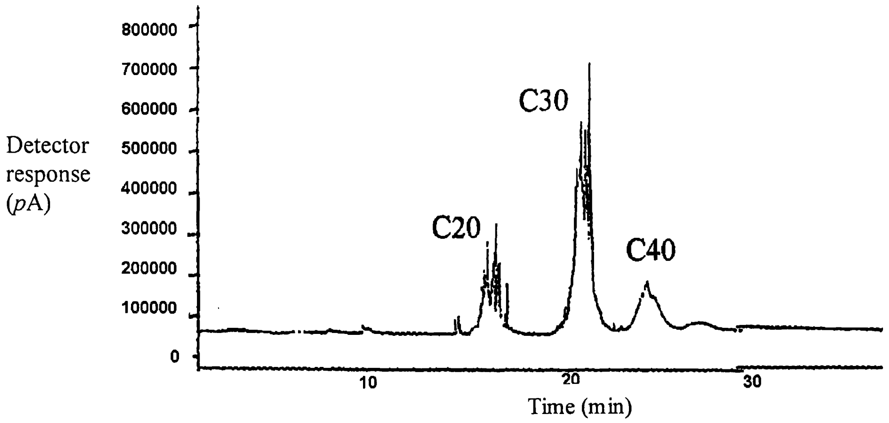

Figure 2. Polyalphaolefin obtained by commercial BF_3/BuOH technology.

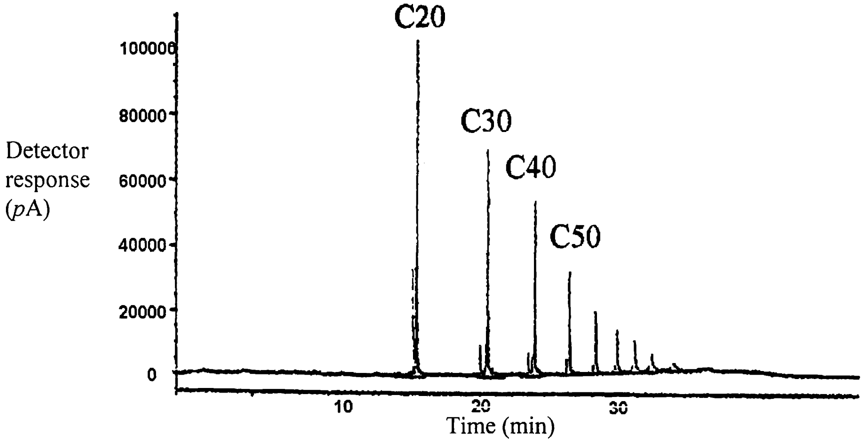

Figure 3. Polyalphaolefin obtained by using metallocene catalyst technology.

Figure 1 clearly shows that the product obtained when using ionic liquids as catalyst displays a large amount of isomerisation within a specific oligomer fraction, while the metallocene catalyst technology (Figure 3) delivers a range of very specific isomers. The oligomer distribution pattern also varies markedly, depending on the chosen catalyst system.

An approximately 4 cSt (viscosity at 100°C) polyalphaolefin (PAO) sample was subsequently isolated from all reaction products by shortpath distillation, and the viscosity properties determined (*14*). These results are compared in Table I:

Table I. Viscosity Properties of PAO Samples

Property	*1-Decene PAO (Ionic Liquid)*	*1-Decene PAO (BF_3/BuOH)*	*1-Decene PAO (Metallocene)*
Viscosity @ 40°C (cSt)	16.02	16.60	15.60
Viscosity @ 100°C (cSt)	3.69	3.83	3.82
Viscosity index (VI)	117	126	141

The viscosity index (VI) is an indication of the viscosity change displayed by a lubricant at different temperatures. Higher VI values show that less viscosity change take place, and therefore indicate higher quality lubricants. The VI displayed by the PAO synthesised using the ionic liquid catalyst compares unfavorable to PAOs prepared from 1-decene using either BF_3/BuOH or metallocene technologies. The PAO prepared using a metallocene catalyst would therefore represent the highest quality PAO (judged only by VI value), followed by the PAO produced by BF_3/BuOH catalyst technology (the benchmark PAO in industry).

Ionic Liquids as Solvent for Olefin Oligomerisation Catalyst Systems

Chromium-catalyzed Trimerisation of Ethylene / Longer Chain α-Olefins

Linear ethylene trimerisation is an important technology for the future commercial production of 1-hexene, used as a co-monomer component for low density polyethylene. Current market trends indicate that the world demand for 1-hexene will exceed world production by the year 2004. The conventional route to 1-hexene is *via* oligomerisation of ethylene using alkylated metal catalysts. During this oligomerisation process, 1-hexene is coproduced along with a wide spectrum of linear alpha olefins displaying even-numbered carbon chain lengths (*15*).

The first selective formation of 1-hexene was reported in literature in 1977 by Manyik *et al* (*16*). In this case, 1-hexene was reported as an oligomeric by-product in a Cr-based ethylene polymerisation system. Phillips Corp. subsequently made a significant impact with regard to the development of a chromium-based process for the trimerisation of ethylene to 1-hexene in high yield (*17*), as shown in Figure 4.

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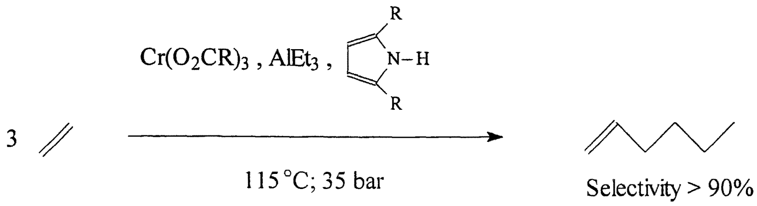

Figure 4. Chromium-based trimerisation of ethylene to 1-hexene.

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Very little is known about the mechanism as well as the nature of the active species in the chromium-catalysed system. Briggs proposed the following catalytic cycle for 1-hexene formation (Figure 5), based on metallacyclic intermediates (*7*):

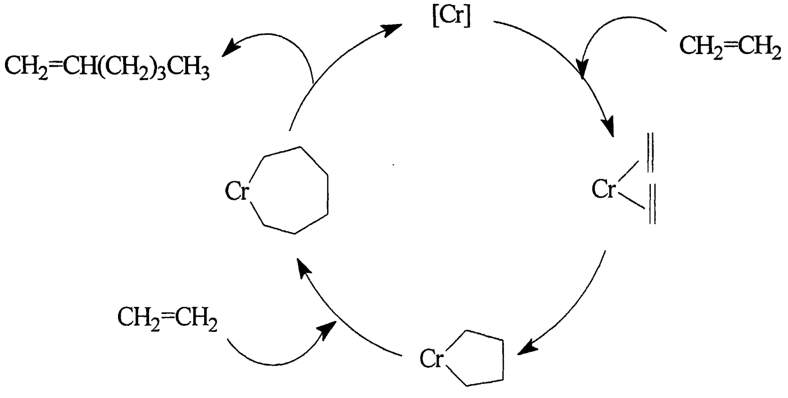

Figure 5. Catalytic cycle for 1-hexene formation. (Reproduced with permission from reference 7. Copyright 1989 The Royal Society of Chemistry, London.)

Subsequent investigations into the possibility of utilising these chromium-based systems together with α-olefins, showed that selective trimerisation (to a mixture of isomers) took place regardless of olefin chain length (*14*) (see Figure 6). These observations are similar to the recently reported results for the selective trimerisation of α-olefins with triazocyclohexane complexes of chromium (*18*). These trimers of long chain α-olefins are useful compounds for lubricant / additive applications, as well as intermediates for various specialty chemicals and pharmaceutical application areas.

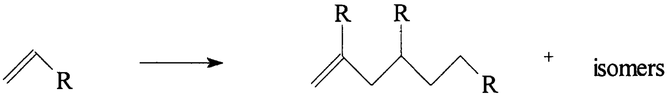

Figure 6. Selective chromium-catalysed trimerisation of longer chain olefins.

i) Ethylene Trimerisation in Ionic Liquids

The use of biphasic ionic liquid systems as a novel way to recover and recycle the chromium catalyst complex during ethylene and longer chain olefin trimerisation was subsequently investigated (*19*). Additional benefits of biphasic systems have previously been shown to be easy separation of products and stabilization of the active catalyst, leading to higher activities and selectivities (*20*).

Various ionic liquids were initially screened to evaluate catalytic activity of the chromium complex (Phillips) in these ionic liquids. Combinations of cations (imidazolium compounds with different alkyl chain lengths, as well as pyridinium compounds) and various anions (e.g. PF_6^-, BF_4^- and $N(SO_2CF_3)_2^-$) were evaluated. No activity was observed in the specific neutral ionic liquids investigated. In addition, different acid strengths of the chloroaluminate ionic liquid [bmim][$AlCl_4$] were evaluated, but again no chromium catalyst activity was observed.

The synthesis of trialkylaluminium-derived ionic liquids and subsequent evaluation for trimerisation catalyst activity eventually led to positive results. The ionic liquid [bmim][Et_3Al-Cl] was chosen as the ionic liquid of choice, and the selective trimerisation of ethylene using the Phillips chromium-based catalyst system was demonstrated. The initial results achieved are compared in Table II to typical results achieved when using a homogeneous chromium catalyst system (cyclohexane as solvent).

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Table II. Homogeneous and ionic liquid ethylene trimerisation results (batch results)

Trimerisation Results	*Ethylene trimerisation in [bmim][Et$_3$Al-Cl]**	*Typical homogeneous ethylene trimerisation*
Catalyst activity (g Product / g Cr / hr)	9 602	35 000
Selectivity C6 (mass %)	62.1	95.0
Selectivity 1-hexene (mass %)	80.7	97.0
Polymer product (mass %)	< 0.5	< 0.5

* *Pre-activated chromium complex dissolved in ionic liquid*

The results show that significantly higher catalyst activity, as well as higher selectivities to the desired product are achieved in the homogeneous reaction. Lower selectivities achieved in the ionic liquid could possibly be adressed by optimising the solubility of 1-hexene in the ionic liquid, in order to minimize consecutive reactions responsible for the formation of higher oligomers.

GC analysis of the reaction product obtained using an ionic liquid was compared to an analysis of the standard homogeneous reaction. The linearity of products is compared in Table III, while the composition of the linear fractions is compared in Table IV.

Table III. Linearity of C6 fractions

C6	*Ionic liquid reaction (mass %)*	*Homogeneous reaction (mass %)*
Linear C6	99.7	99.9
Branched C6 products	0.3	0.1

Table IV. Composition of the linear C6 fractions

C6	*Ionic liquid reaction (mass %)*	*Homogeneous reaction (mass %)*
1-Hexene	82.4	97.5
2-Hexene (*cis* and *trans*)	12.5	2.3
3-Hexene + hexane	5.1	0.2

The linearity of the reaction product obtained in the biphasic ionic liquid reaction compares well to the homogeneous reaction (99.7 *vs* 99.9 %). It is however clear from the composition of the linear fraction that the 1-hexene content in the case of the ionic liquid reaction, is significantly lower when compared to the homogeneous case (82.4 *vs* 97.5 %). Isomerisation could possibly be caused by the high triethylaluminium content of the ionic liquid.

Various optimisation reactions were carried out. High stirring speeds (> 10 000 RPM) and high ethylene pressure (50 bar) led to some improvement in catalyst activity; 1-hexene selectivities remained however largely unchanged. Other parameters that were investigated included temperature, the addition of halogen sources and co-solvents, the excess of Et_3Al added during ionic liquid synthesis, as well as the length of the alkyl chain on the cation. The use of tri-alkylimidazolium ionic liquids led to improvement in the catalyst activity obtained, while comparable C6 and 1-hexene selectivities were observed when compared to results obtained with [bmim][Et_3Al-Cl]. These results can be regarded as the optimum results in this specific ionic liquid, and are shown in Table V.

Table V. Effect of using [trialkylimidazolium]-derived *vs* [dialkylimidazolium]-derived ionic liquids during ethylene trimerisation*

Trimerisation Results	*[1-ethyl-2,3-dimethylimidazolium] [Et_3Al-Cl]*	*[1-butyl-3-methyl-imidazolium] [Et_3Al-Cl]*
Catalyst activity (g product /g Cr/ hr)	25 000	10 000
Selectivity C6 (mass %)	75.0	77.0
Selectivity 1-hexene (mass %)	87.0	87.0

* *Ratio Cr cat.: 2,5-dimethylpyrrole : Et_3Al = 1 : 10 : 20; 50 bar; 115 °C, 30 min.*

The lower activity obtained when using the dialkylaluminium-derived ionic liquid can possibly be explained by the possibility of hydrogen bonding at the 2-position on the dialkylaluminium cation, as well as carbene formation (*21*) that could cause catalyst deactivation.

ii) Longer Chain α-Olefin Trimerisation in Ionic Liquids (22)

Preliminary investigations into the chromium-catalysed trimerisation of long chain olefins (using the Phillips catalyst system) show promise. 1-Decene

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trimerisations performed in an ionic liquid ([bmim][Et_3Al-Cl]) using the Phillips catalyst system are compared to homogeneous results in Table VI:

Table VI. 1-Decene trimerisation results obtained homogeneously *vs* ionic liquid results*

Trimerisation Results	*Homogeneous*	*Ionic liquid [bmim][Et_3Al-Cl]*
Conversion (C10 → product) (mass %)	3.0	46.0
C30 (trimer) selectivity (mass %)	67.0	91.0

* *Unoptimised reaction conditions. Ratio Cr cat. : 2,6-dimethylpyrrole : Et_3Al : olefin = 1 : 7 : 20 : 200; 25 °C; 24 hr*

Although these results are not optimised, the biphasic ionic liquid reaction shows significantly higher olefin conversions as well as trimer selectivity.

The C30 fraction obtained from the 1-decene trimerisation was isolated in order to obtain viscosity properties, to evaluate the product's possible application as PAO synthetic lubricant. The viscosities are compared to a commercial product in Table VII:

Table VII. Comparison of PAO viscosity properties obtained

Property	*1-Decene PAO (chromium)*	*1-Decene PAO (BF_3/BuOH)*
Viscosity @ 40°C (cSt)	12.31	16.60
Viscosity @ 100°C (cSt)	3.21	3.83
Viscosity index (VI)	130	126

The C30 fraction isolated from the chromium-catalyzed trimerisation reaction mixture, displays a lower viscosity at 100°C when compared to the commercial product (3.21 *vs* 3.83 cSt). The viscosity index (VI) is favorably high (130), which suggests that this could be a superior PAO product.

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Nickel-catalysed Oligomerisation of Ethylene / Longer Chain α-Olefins

Various well-researched examples describing the nickel-catalysed oligomerisation of ethylene / longer chain α-olefins in ionic liquids are found in literature. To complete the olefin oligomerisation picture described in this chapter, these results are summarised briefly:

The selective oligomerisation of ethylene to α-olefins by cationic nickel catalysts in hexafluorophosphate ionic liquids was carried out successfully, and a higher oligomerisation activity of the system is reported when compared to the homogeneous reaction (*23*). These results are the subject of a detailed discussion in a separate chapter by Peter Wasserscheid.

IFP initially developed the industrially applied homogeneous Dimersol process for the dimerisation of propene or *n*-butenes to iso-hexenes and iso-octenes. The C_6 intermediates (e.g. 2,3-dimethylbutenes) can be used as starting alkenes for the production of fine chemicals, or for high-octane number olefinic gasoline blending. The C_8 intermediates are used for iso-nonanol manufacture (by hydroformylation), which can be esterified to yield dialkylphthalates, to be used for PVC plasticizers. The dimerisation is carried out without any solvent, using a cationic nickel complex ([$LNiCH_2R'$][$AlCl_4$], where R = PR_3) (*24*).

The Difasol process was subsequently developed where the cationic nickel complex was dissolved in an acidic chloroaluminate ionic liquid (e.g. [1-butyl-3-methylimidazolium]Cl-$AlCl_3$-$EtAlCl_2$). It was found that the ionic liquid stabilised the active nickel species, and the biphasic system led to reduced catalyst cost and disposal. Compared to the homogeneous process, the ionic liquid process led to better selectivity to the desired dimers (90 – 95% *vs* 85% for the homogeneous process). The high selectivity can be ascribed to the lower miscibility of dimer products in the ionic liquid, minimizing consecutive reactions responsible for the formation of for instance trimers. The conversion of butenes was found to be between 70 and 80% (even when the butenes are diluted with inert substrates), comparable to the 80% conversion obtained in the homogeneous system (*25*).

Linear dimerisation of olefins produces highly desirable intermediates for the production of various high value products, for instance C_9 plasticizers. Buffered ionic liquids were used together with a catalyst known to produce linear dimers from 1-butene (based on square planar Ni-*O,O'* chelating systems, with an easily replaceable group such as cod) (*26*). Slightly acidic 1-butyl-4-methylpyridiniumchloroaluminates were buffered with weak organic bases such as pyrrole, *N*-methylpyrrole and chinoline, and used as solvents for the linear

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dimerisation of 1-butene by the described Ni complexes. When compared to the homogeneous reaction performed using toluene as solvent, a significant enhancement of catalyst activity was observed, together with the retention of both dimer selectivity and product linearity as well as the advantage of easy catalyst recovery and recycle.

Conclusion

The use of ionic liquids during olefin oligomerisation shows promise for the development of industrially viable and environmentally friendly processes. The achievement of higher catalyst activities and selectivities in ionic liquids *vs* the conventional homogeneous process has already been demonstrated in specific cases, and further optimisation could lead to potential commercial application (as shown by IFP's nickel-catalysed Difasol process).

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Chapter 13

Ionic Liquids for the Nuclear Industry: A Radiochemical, Structural, and Electrochemical Investigation

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The applicability of ionic liquids within the nuclear industry has been investigated. The radiation stability of ionic liquids containing dialkylimidazolium cations has been tested through with alpha, beta and gamma irradiation. The results of these tests suggest that imidazolium salts have stabilities similar to alkylbenzenes and greater than tetrabutylphosphate / odorless kerosene (TBP/OK) mixtures. The oxidative dissolution of uranium dioxide and the anodic dissolution of uranium metal and plutonium metal have been carried out in various ionic liquid media

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

Introduction

Academic and industrial interest in ionic liquid technologies has increased significantly over the past decade. A number of reviews covering most aspects of research into ionic liquids have recently appeared. (1-5) Recent publications point to the growing interest in the use of the behaviour of uranium species in ionic liquids by the nuclear industries. Much of the earliest work naturally focused on the behaviour of uranium species in chloroaluminate ionic liquids. De Waele *et al.*, (6, 7) carried out the first investigation of uranium in acidic mixture of aluminum chloride and butylpyridinium chloride. The dioxouranium(VI) tetrachloride complex $[UO_2Cl_4]^{2-}$ has been studies in basic mixture of aluminum chloride and $[C_2mim]Cl$. (8, 9) Dai *et al.*, (10) investigated the spontaneous conversion of UCl_6^- to UCl_6 in chloroaluminate ionic liquids. The dependence of the solubility of the uranium chloride complexes upon the organic cation in basic chloroaluminate ionic liquids has also been reported by Dai *et al.* (11) C.J. Anderson et al., (12) thoroughly examined the redox behaviour of oxouranium chloride complexes in acidic chloroaluminate ionic liquids. Recent work by Costa *et al.*, (13) has investigated the behaviour of dioxouranium(VI) and dioxoplutonium(VI) species in acidic chloroaluminate ionic liquids. Critical mass calculations carried out by Harmon *et al.*, on two plutonium metal/ionic liquid mixtures have recently been published. (14)

Work by Dai *et al.*, (15) and Rogers *et al.*, (16, 17) has demonstrated that room temperature ionic liquids could be used in solvent extraction of metal species from acidic aqueous media. This is an area of great significance to the nuclear industry which currently uses solvent extraction in the PUREX process for processing spent nuclear fuel. (18)

A series of patents has emerged jointly from The Queen's University of Belfast (QUB) and British Nuclear Fuels plc (BNFL) dealing with the use of ionic liquids in areas such as nuclear fuel reprocessing and the treatment of historical nuclear waste. (19-23) This chapter will discuss many aspects of the ongoing research into this area being conducted by QUB and BNFL. Three phases of this investigation will be discussed: the series of tests carried out to determine the radiation stability of ionic liquids containing the 1-alkyl-3-methylimidazolium cation $[C_nmim]^+$;[1] the oxidative dissolution of uranium dioxide in ionic liquid media; and the behaviour of uranium and plutonium species produced through the anodisation of the respective metal.

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[1] In this chapter, the 1-alkyl-3-methylimidazolium ionic liquids and solids will be referred to as $[C_nmim]X$ where *n* is the number of carbon in the 1-alkyl group and X is either chloride or nitrate.

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Radiochemical Stability of Ionic Liquids

If ionic liquids are to be used by the nuclear industry, they must be radiation stable: that is, they must not undergo significant degredation due to radiolysis upon exposure to radiation levels. A bench mark of comparison would be the solutions of tributylphosphate in odorless kerosene (TBP/OK) currently used in the Purex process for reprocessing spent nuclear fuel. Radiolysis of TBP is known to produce products which interfere with the Pruex process.

All of the ionic liquids tested for radiation stability were subjected to a radiation dose of 400 kGy. This is the average dose experienced by TBP/OK over its lifetime in the THORP Purex processing plant in Sellafield, U.K., and was the radiation dose used in a recent study on the radiation stability of TBP/OK mixtures recently carried out by BNFL. ^{1}H and ^{13}C NMR spectroscopy[2] was used to analyze all samples which underwent radiation stability tests. Spectra recorded before and after testing were compared to determine if any radiolysis had occurred. It should be noted that NRM spectroscopy will be unable to identify if conversion below one percent. However, this should be sufficient for comparison to solution of TBP/OK which underwent up to fifteen percent conversion under similar conditions. The ionic liquids tested included 1-butyl-3-methylimidazolium nitrate $[C_4mim][NO_3]$, 1-ethyl-3-methylimidazolium chloride $[C_2mim]Cl$ and 1-hexyl-3-methylimidazolium chloride $[C_6mim]Cl$.

Gamma Irradiation[3]

Samples of $[C_4mim][NO_3]$ and $[C_2mim]Cl$ underwent gamma radiation testing. The color of the ionic liquids exposed to gamma radiation was seen to slightly darken as a result of radiation. However, no changes were observed in the NMR spectra recorded before and after irradiation, suggesting that less than one per cent of the ionic liquid underwent conversion.

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[2] NMR spectroscopy was carried out by Mr. R. Murphy at Queen's University Belfast using a Bruker Advance DRX 500 NMR spectrometer.

[3] Gamma radiation tests were performed at the J. J. Thomson Irradiation Laboratory. The Cobalt 60 Gamma Facility was used as the gamma source. The ionic liquids were subjected to four different doses of gamma irradiation using three different dose rates, up to a maximum dose of 400 kGy. Dosimetry was performed by a N. E. Technology Ionex 2500/3 Ion Chamber dose rate meter calibrated and traceable to NPL Standard.

Beta Particle Irradiation[4]

Only $[C_4mim][NO_3]$ underwent beta particle irradiation. Some transient species were detected between pulses of radiation.[5] During irradiation, spectral peaks were observed to grow and decay in series, indicating the formation and decay of a series of radiolysis products. It is believed that an end product forms from these transient species which is stable, but the identity of this stable species remains uncertain as no simple means of analysis was available. A comparison of the NMR spectra recorded before and after irradiation suggested that less than one per cent of the ionic liquid underwent conversion.

Alpha partical irradiation[6]

Samples of $[C_4mim][NO_3]$ and $[C_6mim]Cl$ underwent alpha particle irradiation. By analysing the head space for evolution of volatiles, the degradation of the ionic liquids could be monitored. No measurable peaks from organic fragments were observed; the only peak which changed during radiolysis was the yield of hydrogen. When the mass spectrometer was set up to measure hydrogen continuously, there was a definite correlation between the alpha

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[4] Beta particle tests were performed at the Paterson Institute for Cancer Research. A Vickers 10 MeV electron LINAC was used to produce a pulsed beam of electrons. The dose per pulse was calibrated using a Fricke dosimeter. A 0.1 μs pulse delivered a dose of 10 Gy and a 5 μs pulse gave a dose of 160 Gy. The ionic liqued was sampled in a quartz capillary cell and irradiated with a dose equivalent to 400 kGy over 40 minutes.

[5] An on-line UV/VIS/IR spectroscope was used to analyse the sample during irradiation. Time-resolved absorption spectrophotometry measurements were carried out in the 25 mm quartz capillary cell using either a photomultiplier detector system or a 10 diode multi-wavelength detection system. Fast transient studies were performed using a Si diode based system and a pulsed analysing light source. Absorbance was generally observed in the wavelength range between 400 and 600 nm.

[6] Alpha particle tests were performed at AEA Technology. A 4 mV Tandem Van de Graaff was used to produce a beam of alpha particles with a maximum energy of 15 MeV. An irradiation cell was designed so that the energy of the helium ions reaching the sample was similar to that of the alpha particles from plutonium (approximately 5.1 MeV). During the irradiation experiments, the sample head space was 'sniffed' and analysed by mass spectroscopy to facilitate the identification of any volatile species produced.

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particle current and the hydrogen yield, indicating that the hydrogen was the product of ionic liquid radiolysis.

A comparison of hydrogen yields from selected compounds shows that alkanes have the highest yield ($G(H_2)$ = 5.6-5.9 molecules / 100 eV for cyclohexane), followed by alkyl-substituted aromatics (0.2 molecules / 100 eV for isopropylbenzene) and aromatic compounds (0.038 molecules / 100 eV for benzene). Nitrogen heterocycles are very stable with imidazole amongst the most stable (0.03 molecules / 100 eV). The values of $G(H_2)$ determined for the $[C_4mim][NO_3]$ and $[C_6mim]Cl$ were 0.65 and 0.72 molecules / 100 eV, which suggests that their radiation stabilities are similar to that of substituted aromatics.

Behaviour of Dioxouranium(VI) in Ionic Liquids

The Purex process begins with the dissolution of uranium dioxide into a solution of nitric acid, followed by extraction of uranium (and plutonium) species into a TBP/OK diluent. For this reason, it was decided initially to investigate the dissolution of uranium oxides in nitrate-based ionic liquids.

Oxidative Dissolution of Uranium Dioxide

Uranium(IV) dioxide (1 g) was oxidatively dissolved in $[C_4mim][NO_3]$ (5 g) with concentrated nitric acid (10% of the reaction volume) at 70 °C. This led to the formation of bright yellow solutions. A structured absorbance band at 435 nm in the UV-VIS spectrum of the solution confirmed the presence of a dioxouranium(VI) species. Upon cooling, it was not uncommon for a yellow powder to precipitate from the reaction medium. The yellow powder was recrystallised from ethanenitrile and identified as 1-butyl-3-methylimidazolium μ_4-(*O*,*O*,*O*′,*O*′-ethane-1,2-dioato)-bis[bis(nitrato-*O*,*O*)dioxouranate(VI)][7] (Figure 1) by single crystal x-ray diffraction.[8] Comparison of the X-rbay powder

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[7] Crystal Data for $[C_4mim]_2[\{UO_2(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ (**1**): M = 1154.56, monoclinic, space group $P2_1/c$, a = 15.452(2) Å, b = 20.354(3) Å, c = 10.822(4) Å, β = 106.84(2)°, U = 3258(1) $Å^{-3}$, Z = 4, μ = 10.023 mm^{-1}, R_{int} = 0.0788. A total of 5100 reflections were measured for the angle range $4° < 2\theta < 45°$ and 4033 independent reflections were used in the refinement. The final parameters were $wR2$ = 0.1459 and $R1$ = 0.0584 $[I > 2\sigma I]$.

[8] Data were collected on a Siemens P4 diffractometer using the XSCANS software with omega scans. A crystal was mounted on to the diffractometer at low temperature under dinitrogen at *ca.* 120 K. The structure was solved using direct methods with the SHELXTL program package.

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diffraction pattern[9] of the powder sample with the theoretical pattern generated from the crystal structures shows them to be identical.

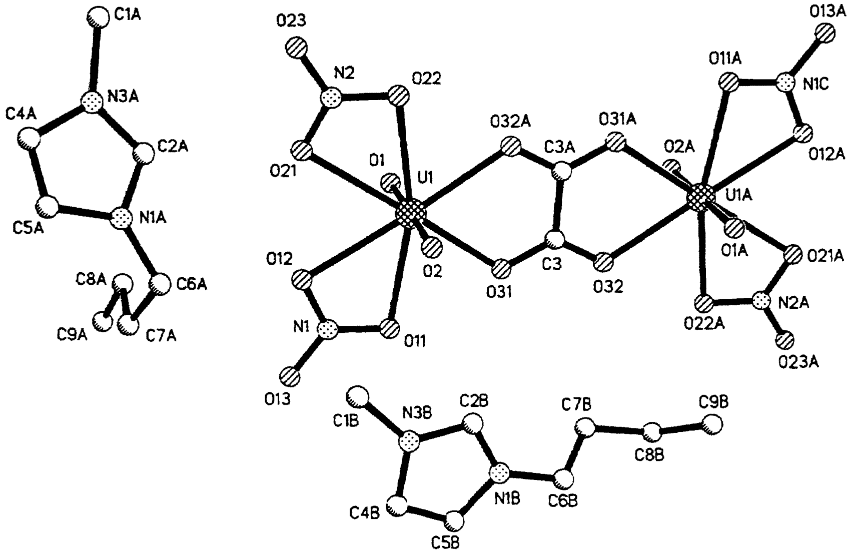

Figure 1. Structure of $[C_4mim]_2[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ *as determined by single crystal x-ray crystallography. The hydrogen atoms have been removed for clarity.*

It was suspected that the source of the bridging oxalate moiety was an organic species inadvertently coming into contact with the reaction mixture. As acetone is a common organic solvent used in the preparation of ionic liquids and the cleaning of glassware and may be oxidised by nitric acid, it was suggested that this might be the oxalate source.

In the ^{13}C NMR spectra of $[C4mim]_2[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$, there are eight peaks arising from the eight carbon atoms in the $[C_4mim]^+$ cation plus a singlet peak at 177 ppm arising from the oxalate carbon atom. When the oxidation of uranium(IV) oxide by nitric acid in $[C_4mim][NO_3]$ was carried out in the presence of either $(CH_3)_2{}^{13}CO$ or $(^{13}CH_3)_2CO$ (*ex* Aldrich), the peak at 177 ppm in the ^{13}C NMR spectra showed a significant increased magnitude relative to the other peaks in the ^{13}C NMR spectra with respect to samples of $[C_4mim]_2[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ prepared using unlabelled acetone. Further experiments showed that the oxalate source, acetone, can be added either prior to or after oxidative dissolution of UO_2 has occurred. In both cases, the ^{13}C NMR spectra again have a peak at 177 nm.

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[9] Powder diffraction measurements were performed on a Siemens D5000 powder diffractometer in continuous mode with step size of 0.02° and step time of 1 s.

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Structure

The k^3-weighted U L(III) edge EXAFS[10] oscillations and their corresponding Fourier transforms for the complex in the solid phase and dissolved in $[C_4mim][NO_3]$ ionic liquid are shown in Figures 2 and 3, respectively. The EXAFS and single-crystal XRD structural parameters are summarized in Table 1.

Table 1. Structural parameters of the $[bmim]_2[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ complex in a solid boronitride (BN) matrix (EXAFS), dissolved in $[C_4mim][NO_3]$ in a graphite matrix (EXAFS) and of the crystal (XRD).

	complex in BN			*complex in $[C_4mim][NO_3]$*			*crystal structure*
	R/Å	*σ^2*	*fit*	*R/Å*	*σ^2*	*fit*	*R/Å*
U=O	1.78	0.011		1.76			1.74
U-O(ox)	2.35	0.021		2.37			2.46
U-O(n)	2.52	0.017		2.55			2.49
U-N	2.96	0.006	24.57	2.93		25.99	2.90
U-C	3.28	0.011		3.41			3.25
U-O(n)	4.28	0.002		4.18			4.12
U-O(ox)	4.60	0.010		4.67			

The crystal structure of the complex, shown in Figure 1, shows that there are a number of multiple scattering pathways that will contribute significantly to the final fit. The most important include backscattering from the uranyl component and along the U-O-N-O-U pathway. The two largest peaks noted in the Fourier transforms of the EXAFS data, shown in Figures 2 and 3, can be attributed to the uranyl (U=O) shell and the second peak is a convolution of both the bidentate oxygen shells from the nitrate and oxalate ligands. Although the uranium atom is

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[10] The solid sample was prepared by thorough grinding with the matrix, boron nitride powder, (Aldrich) and pressing into a disk (~ 5mm), which was loaded into an in-situ EXAFS cell. The ionic liquid solution samples were prepared by mixing the solutions with graphite to form a paste which could be spread between two graphite disks. The EXAFS data was obtained at the Synchrotron Radiation Source (SRS) in Daresbury, U.K., at Station 9.2. The transmission detection mode was used with two ionization chambers filled with argon. The spectra were recorded at the uranium L(III) edge (17,166 eV) using a double crystal Si(220) monochromator set at 50 % harmonic rejection. Background subtraction of the spectra were carried out using the EXCALIB and EXBROOK programs and the data fitted using the EXCURV98 program.

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a strong backscatterer, no significant scattering above 5 Å is observed in the data which indicates that an interaction between the two uranium atoms of the dimer is not seen. Interactions between uranium atoms have only been noted in dimeric structures with U-U distance below 4 Å. The EXAFS data for the ionic liquid sample containing digested uranium dioxide in an acetone environment has a fit of 20.52 % for the dioxouranium(VI) nitrato oxalato structure $[C_8H_{15}N_2]_2[\{UO_2(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$. As the complex is soluble in the $[C_4mim][NO_3]$ ionic liquid, not all of the complex may have precipitated and some may remain in the ionic liquid.

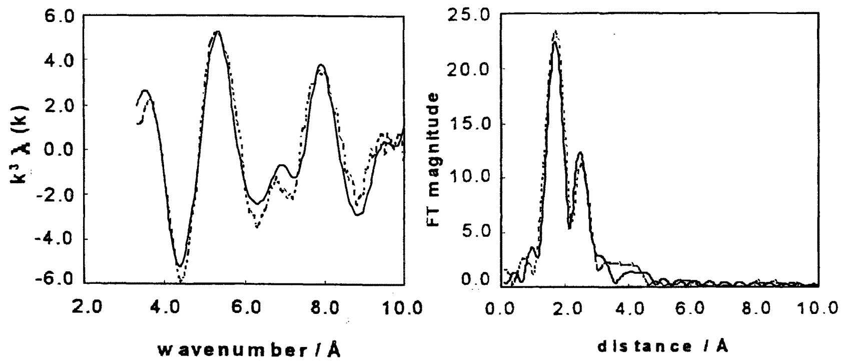

Figure 2. The k_3-weighted U L(III) edge EXAFS oscillations and their corresponding Fourier transforms for the complex dissolved in $[C_4mim][NO_3]$ ionic liquid.

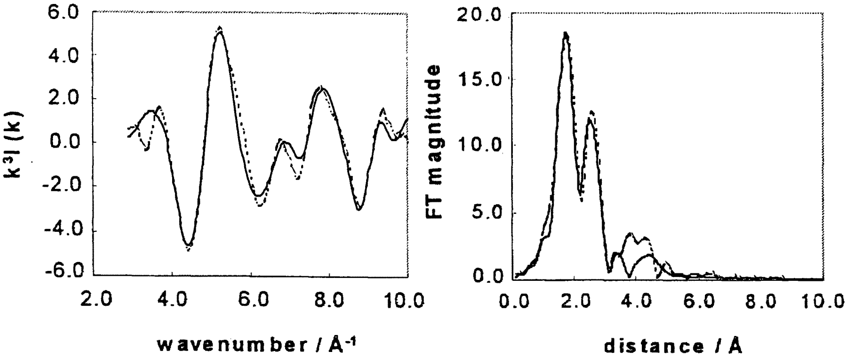

Figure 3. The k^3-weighted U L(III) edge EXAFS oscillations and their corresponding Fourier transforms for the complex in the solid phase.

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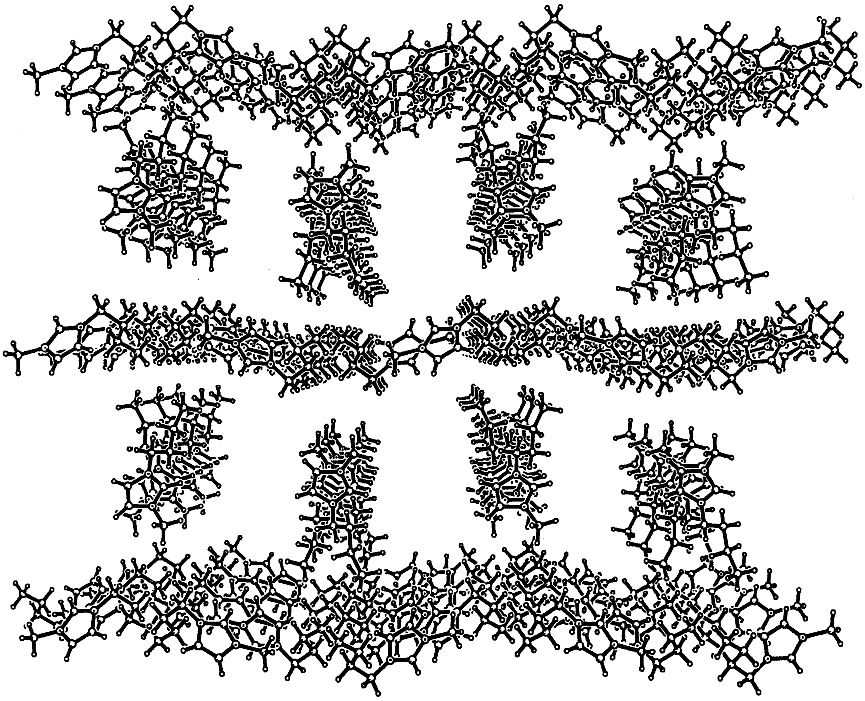

Figure 4. Arrangement of $[C_4mim]^+$ cations in the $[C_4mim]_2[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ crystal as determined by single crystal X-ray crystallography. The $[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ moieties are located inside the rectangular holes formed by the $[C_4mim]^+$ cations, and have been left our for clarity.

X-ray analysis of $[C_4mim]_2[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ shows the unit cell contains four $[C_4mim]^+$ cations and two independent $[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ moieties both of which are located about inversion centers. The $[C_4mim]^+$ cations are arranged such that they produce large channels in which the anions are located (Figure 4). Thus the anions effectively act as a template for the cations. This arrangement of $[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ groups is unique to this compound. In the $[(H_5O_2)((NO_2)_2\text{benzo-15-crown-5})_2]_2\text{-}[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ and $[(H_3O)(18\text{-crown-6})]_2\text{-}[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ salts prepared by Rogers *et al.*, (24) the lattice is dominated by the presence of the large crown ether molecules and consequently the $[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]^{2-}$ moieties are oriented at 78.7° and 47.2° to one another respectively. In the $[(C_2N_2H_{10})_2][(UO_2)_2(\mu_4\text{-}C_2O_4)_3\bullet(i\text{-}Me_2CHNHO)_2]\bullet H_2O$ salt reported by Shchelokov *et al.*, (25) the anions still contain the bridging oxalate but there are also two terminal oxalate moieties and two hydroxylamine ligands. The anionic component of salts prepared by Rogers *et al.*, (24) is the same as found in $[C_4mim]_2[\{(UO_2)(NO_3)_2\}_2(\mu_4\text{-}C_2O_4)]$ and the origin of the bridging oxalate moiety is attributed to the presence of impurities in the nitric acid. The preceding ^{13}C NMR experiments indicate that adventitious acetone is the most likely source of the bridging oxalate moiety in their salts but other organic impurities cannot be ruled out.[8]

Electrofining Uranium Metal[11]

Currently, at least two methods of electrochemically processing spent nuclear fuel in high temperature molten salt media are being investigated. In the Argonne National Laboratory (ANL) lithium process, declad oxide fuel is dissolved in a LiCl:KCl eutectic at 773 K. (26) The oxides are reduced to metals in the presence of lithium metal. Uranium is then purified through an electrorefining process: the fuel is oxidised at an anode and purified uranium is deposited at a cathode. The process being developed by the Research Institute of Atomic Reactors (RIAR) in Dimitrovgrad, Russia, operates in a NaCl:KCl melt at 1000 K. (27) In this process, oxide fuel is oxidatively dissolved using chlorine and oxygen gases. Uranium is recovered as UO_2 (which is an electrical conductor at 1000 K) through electrochemical reduction at a carbon cathode.

The substitution of ionic liquid systems which operate at much lower temperatures might eliminate many of the technical and safety concerns involved in pyrochemical processes. The low vapour pressures associated with ionic liquids eliminates the environmental concerns associated with volatile organic solvents. The ability to purify and recycle ionic liquids means that the waste produced in these systems would be decreased. Finally, the combination of ionic and organic properties allows for a variety of different physical, chemical, and

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[11] All electrochemical experiments were carried out with an EG&G PARC Model 283 potentiostat/galvanostat controlled using EG&G Parc Model 270/250 Research Electrochemistry software. Positive feedback iR compensation was employed to eliminate errors due to solution resistance. The non-aqueous reference electrode was a silver wire immersed in a glass tube containing a 0.100 mol L^{-1} solution of $AgNO_3$ in the $[C_4mim][NO_3]$ ionic liquid which was separated from the bulk solution by a Vycor plug. All potentials reported are referenced against the $AgNO_3/Ag$ couple. For voltammetry, the counter electrode was a platinum coil immersed directly in the bulk solution and the working disk electrode was glassy carbon ($A = 7.07 \times 10^{-2}$ cm^2). All experiments were carried out at 90 °C and under a dry dinitrogen atmosphere.

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electrochemical techniques for reprocessing spent nuclear fuel and purification of the reprocessing medium to be explored.

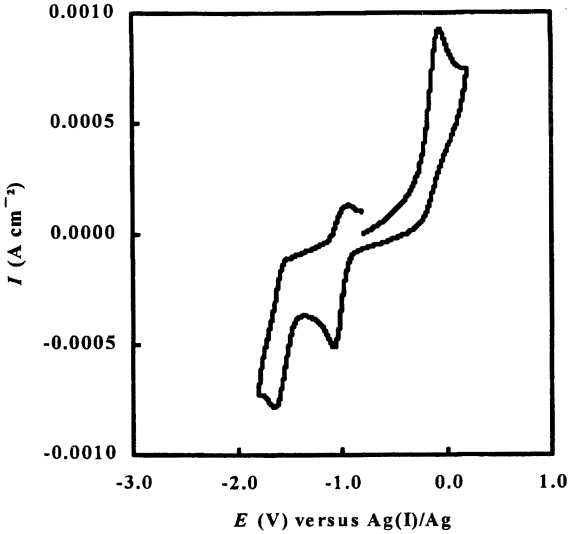

Figure 5. Cyclic voltammogram recorded in a solution of [emim]Cl containing plutonium species produced by anodisation of plutonium metal. T = 90 °C. Scan rate = 0.050 V s^{-1}.

Uranium

Anodisation of a uranium metal plate was carried out in [C_2mim]Cl at 90 °C at an applied potential of +0.3 V versus Ag(I)/Ag at a current around 2 mA. Table 2 shows the mass loss by the uranium anode (ΔWt_U) due to the charge passed (Q_T) during a number anodisation experiments in a variety of ionic liquids and compares the result with the theoretical weight loss ($\Delta Wt_{theory(n=3)}$) for a three electron oxidation of uranium metal. From this data, it is apparent that U(III) is being formed by the anodisation, most likely producing [$C_n$mim]$_3$$UCl_6$. However, from the cyclic voltammograms recorded in the solutions produced by anodisation of uranium (Figure 5 is typical), it is clear that UCl_6^{3-} is not stable in the [C_2mim]Cl. The presence of a $\{UO_2\}^{2+}$ species may be indicated by the reduction wave located around −1.7 V. Other experiments (*vide infra*) confirm the presence of the $[UO_2Cl_4]^{2-}$ and $[UCl_6]^{2-}$ but no U(III) species, indicating that the U(III) species formed during electrolysis undergoes chemical reactions, perhaps reacting with residual water in the ionic liquid. The presence of water in [C_2mim]Cl and the reactivity between water and uranium make the electrochemical behaviour of uranium in these ionic liquids much different than

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that observed in chloroaluminates,[8] which are virtually water-free due to their reactivity with water.[1]

Table 2. Anodisation data for uranium metal.

Ionic Liquid	Q_T / C	ΔWt_U / g	$\Delta Wt_{theory,(n=3)}$ / g
$[C_4mim][NO_3]$	1000	0.78	0.82
$[C_6mim]Cl$	1235	1.01	1.02
$[C_6mim]Cl$	236	0.19	0.19
$[C_6mim]Cl$	624	0.64	0.51
$[C_6mim]Cl$	200	0.17	0.16
$[C_6mim]Cl$	693	0.55	0.57

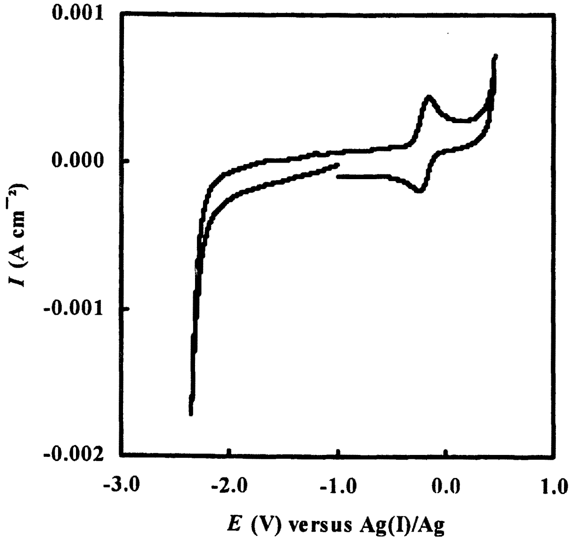

Figure 6. Cyclic voltammogram recorded in a solution of $[C_2mim]Cl$ containing uranium species produced by anodisation of uranium metal. T = 90 °C. Scan rate = 0.050 $V s^{-1}$.

Plutonium

Contact between plutonium metal and $[C_2mim]Cl$ at 90 °C resulted in a spontaneous reaction which probably involved the oxidation of Pu by the $[C_2mim]^+$ cation. This is to be expected because the high activity of Pu. Anodisation of Pu was carried out in $[C_2mim]Cl$ at 90 °C at E_{app} = -1.8 V versus

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$AgNO_3/Ag$. The spontaneous reaction between Pu and $[C_2mim]^+$ which occurred simultaneously made it impossible to compare the charge passed and the mass loss to determine the oxidation state of the plutonium species produced during anodisation. Cyclic voltammetry (Figure 6) performed on solutions generated by the anodisation of Pu appear indicate that Pu(III) was generated during anodisation and demonstrate the quasi-reversible oxidation of Pu(III) to Pu(IV) at potentials around O V versus $AgNO_3/Ag$. The reduction of Pu(III) to plutonium metal is not possible in the $[C_2mim]Cl$ ionic liquids as the Pu(III)/Pu electrochemical couple falls outside the cathodic window of the solvent (approximately –2.3 V versus $AgNO_3/Ag$).

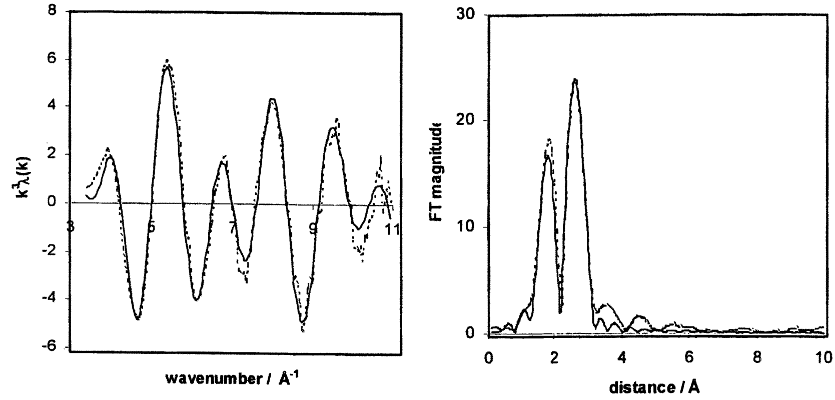

Figure 7. The k^3-weighted U L(III) edge EXAFS oscillations and their corresponding Fourier transforms for $[C_2mim]Cl$ containing species of uranium produced through anodisation of uranium metal.

Structure

Samples of ionic liquid after the anodization of uranium metal were studied using EXAFS to establish both the oxidation state and the speciation of uranium in the ionic liquid. It is assumed when the uranium metal is anodized it is in the +3 oxidation state in the ionic liquid. It has been shown electrochemically that the uranium is actually in a mixture of oxidation states. The original model used to fit the EXAFS data was $[UCl_6]^{2-}$ although the edge-jumps for the samples was 17166.6 eV, slightly higher than the edge jump for uranium(IV). The pseudoradial distribution functions for each of the ionic liquids (Figure 7) show two peaks, indicating two shells, and the data could not be fitted to the $[UCl_6]^{2-}$ model. It had been suggested that if reduction of the imidazolium ring has occurred, dealkylation of the alkyl-methylimidazolium radical formed may occur [the resulting alkyl radical being more stable than a methyl radical]. The EXAFS could not be fitted to a model with methylimidazole ligands on the uranium centre. Therefore, if reduction of the ionic liquid occurs, the resulting species do not interact with the uranium centre. The best model for the EXAFS data was a mixture of both $[UCl_6]^{2-}$ and $[UO_2Cl_4]^{2-}$ models which also explained the change in edge jump. As $[C_2mim]Cl$ ionic liquid is renown for being hydroscopic, this may explain the degree of oxidation of the anodized uranium species.

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Conclusions

Studies of the radiolysis of the 1-alkyl-3-methylimidazolium cations has shown that their stability is similar to that of benzene and that they are much more stable than mixtures of TBP/OK under similar irradiation conditions. This is a very promising result if such ionic liquids are to be used in the nuclear industry, especially when coupled with the criticality results of Harmon *et al.* [14]

A means for isolating a uranyl species from the $[C_4mim][NO_3]$ ionic liquid has been demonstrated. The electrotransport of uranium and plutonium, with the aim of electrorefining uranium, has proven difficult, in the $[C_nmim]X$ ionic liquids, due to the positive reduction potential of the $[C_nmim]^+$ cation and the instability of the U(III) species. Organic cations with more negative reduction potentials than $[C_nmim]^+$ may prove more successful in this regards, but will require further radiolysis testing.

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Chapter 14

Nuclear Chemistry and Electrochemistry: Superoxide Ion Electrochemistry in Ionic Liquids

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We have demonstrated that superoxide ion can be generated electrochemically in room-temperature ionic-liquid solvents. Similar superoxide ion chemistry has previously been demonstrated in volatile and environmentally-suspect aprotic solvents such as dimethyl formamide and acetonitrile. However, ionic liquids are non-volatile and should minimize the problems of secondary solvent waste. It is proposed that the resultant superoxide ion can be used to perform low-temperature oxidation of wastes. Low-temperature oxidation of waste solvents can provide a much-needed alternative to high temperature waste incinerators, whose use is greatly complicated by regulatory requirements and locating suitable sites.

Introduction

Superoxide ion chemistry. Sawyer and co-workers (1-3) pioneered work on superoxide ion ($O_2^{\bullet-}$), particularly the direct electrochemical reduction of dissolved oxygen gas in aprotic solvents to form $O_2^{\bullet-}$ according to the following reaction

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

$$O_2 + e^- \rightarrow O_2^{\bullet-} \qquad (1)$$

A comprehensive review of superoxide ion chemistry is given by Sawyer *et al.* (4). Sawyer in the early 1980's investigated this chemistry as a means of destroying organic solvent wastes (3,5). Superoxide ion can be formed directly from solvation of K_2O in aprotic solvents, or electrochemically via direct cathodic reduction of dioxygen (typically E=-1.0V vs, SCE) (23). $O_2^{\bullet-}$ is a strong nucleophile and is rapidly reduced in water to O_2 and hydroperoxide:

$$2\ O_2^{\bullet-} + H_2O \rightarrow O_2 + HOO^- + HO^- \qquad (2)$$

For this reason, generation and utilization of $O_2^{\bullet-}$ must be done in aprotic solvents. Acetonitrile (MeCN), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) are commonly used. To impart sufficient electrical conductivity, a supporting electrolyte such as tetraethyl ammonium perchlorate (TEAP) is dissolved in the solvent. Reagents must be scrupulously dried, but if properly prepared and stored, are stable for extended times.

The superoxide ion can degrade polychlorinated aromatics and PCBs to bicarbonates and chlorides (2,3,6). The mechanism of destruction is thought to be a nucleophilic reaction of $O_2^{\bullet-}$ with the chlorine-carbon bond, as is illustrated for the reaction involving hexachlorobenzene (6):

$$C_6Cl_6 + O_2^{\bullet-} \rightarrow [C_6Cl_6\,O_2^{\bullet-}] \rightarrow C_6Cl_5\,O_2^{\bullet} + Cl^- \qquad (3)$$

$$C_6Cl_5\,O_2^{\bullet} + O_2^{\bullet-} \rightarrow C_6Cl_4O_2 + O_2 + Cl^- \qquad (4)$$

$$C_6Cl_4O_2 + 10\ O_2^{\bullet-} \rightarrow 3\ C_2O_6^{2-} + 2\ O_2 + 4\ Cl^- \qquad (5)$$

$$3\ C_2O_6^{2-} + 3\ O_2 + 3\ H_2O \rightarrow 6\ HCO_3^- + 3/2\ O_2 \qquad (6)$$

The nucleophilic addition of superoxide ion in reaction [3], as well as the reactions [4] and [5], must take place in an anhydrous environment. Kalu and White (6) have determined that PCBs were not completely destroyed in a flow-through reactor due to slow kinetics. In any case, however, the present state of knowledge requires use of volatile aprotic organic solvents, which suggests a serious problem with atmospheric solvent emissions and generation of secondary

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solvent wastes. Casadei *et al.* (7) utilized the methods of Sawyer *et al.* (1-4) to generate stable solutions of $O_2^{\bullet-}$ in MeCN using TEAP as the electrolyte.

The objective of this work is to replace aprotic solvents with ionic liquids as the medium for conducting superoxide ion chemistry. Room Temperature Ionic Liquids (RTILs) are stable mixtures of an organic cation/anion salt with an inorganic salt (8-12). They are directly related to more familiar high temperature molten salts that are used, for example, as heat transfer media.

Holbrey and Seddon (13) have recently reviewed the applications of RTILs as substitute solvents in green chemistry, with an emphasis on organic synthesis. Early work on RTILs in electrochemistry focused on their use as electrolyte for advanced battery systems. More recently, a number of classical organic syntheses have been demonstrated using RTILs, including dimerization of alkenes (14,15) and oligomerization of butene (20-22), which utilize the acid catalyst properties of $AlCl_3$. Neutral ionic liquids containing $[BF_4]^-$ or $[CuCl_2]^-$ are less reactive and do not promote polymerization of alkenes, and have been utilized in homogeneous catalytic hydrogenation of olefins (19, 20). Furthermore, RTILs may provide facile separations in either liquid-RTIL (21) or supercritical fluid/RTIL (22) extractions due to their low volatility and adjustable affinity for water and organic solvents.

With regard to electrochemistry, certain RTILs are electrically stable over a range of 2-4V and higher, are thermally stable, and are resistant to oxidation, including photooxidation in solar cells (23-25). Various electrochemical syntheses have been attempted, including polymerization of arenes to form conducting polymers (26), polymerization of benzene to poly (*p*-phenylenes) (27-29), oligomerization of anthracene (30), and preparation of silane polymer films (31). More fundamental studies on redox reaction kinetics and behavior in RTILs have been done for anthracene (32), methylanthracene (33), and other aromatics (34-36). It is clear that some RTILs can be used to support electrochemistry; as far as we are aware, however, there has been no research on supporting superoxide ion chemistry in these novel solvents.

In this paper we show that superoxide ion can be generated via reaction [1] in room temperature ionic liquid solvents (RTILs). Blanchard and Brennecke (37) showed that halogen-carbon compounds are soluble in RTILs. This finding offers promise that electrochemical oxidation of chlorinated solvents in ionic liquid media may be an environmentally acceptable route for destruction of these pollutants.

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Experimental

Cyclic voltammetry (CV) tests were performed on the aprotic solvent system tetraethylammonium perchlorate (TEAP, 0.1M) in acetonitrile (MeCN) and in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-HFP). TEAP (GFS Chemicals) was dried overnight in a vacuum oven at 40°C, HPLC-grade MeCN (Fisher Scientific) was used as provided, and BMIM-HFP (SACHEM) was dried overnight in a vacuum oven at 50°C. The electrochemistry was performed using an EG&G 263A potentiostat/galvanostat controlled by computer and data acquisition software. The electrode configuration was a glassy carbon working (BAS, 3mm dia.) and a platinum mesh counter (Aldrich) using SCE and Ag/AgCl references (both Fisher Scientific) for the experiments in MeCN and BMIM-HFP, respectively. The MeCN sample was sealed or handled under nitrogen sparge to prevent water contamination, and all BMIM-HFP experiments were performed in a dry glove box under an argon atmosphere. The systems were sparged prior to electrochemical experiments with UHP nitrogen or oxygen fitted through a Drierite gas purification column (W.A. Hammond).

Prior to superoxide ion generation, a nitrogen sparge was used while obtaining a reference voltammogram. Oxygen was then bubbled through the system for 30 minutes to allow sufficient solubilization. Between consecutive CV runs, oxygen was bubbled briefly to refresh the system with oxygen and to remove any concentration gradients. Nitrogen or oxygen sparging was discontinued during the CV data acquisition.

Results and Discussion

Figures 1 shows cyclic voltammograms in: a) 0.1M TEAP/MeCN and b) BMIM-HFP. Reduction currents are positive through out this paper. The CVs were run with nitrogen and oxygen sparging. In MeCN, the presence of oxygen results in a faradic reduction and oxidation peaks at −1.00V and −0.72V vs. SCE, respectively. This CV is consistent with that obtained by Sawyer *et al.* (4) They concluded that the reduction peak is due to the generation of superoxide ion according to reaction [1] and the oxidation peak due to the reverse of reaction [1]. In contrast, the nitrogen baseline showed no such peak, which indicates that the solvent is stable under these conditions and the resulting current is due to the charging of the double layer.

In BMIM-HFP, Figure 1b, the presence of oxygen showed a reduction peak at approximately −0.86V and an oxidation peak at −0.54V vs. Ag/AgCl. Sawyer

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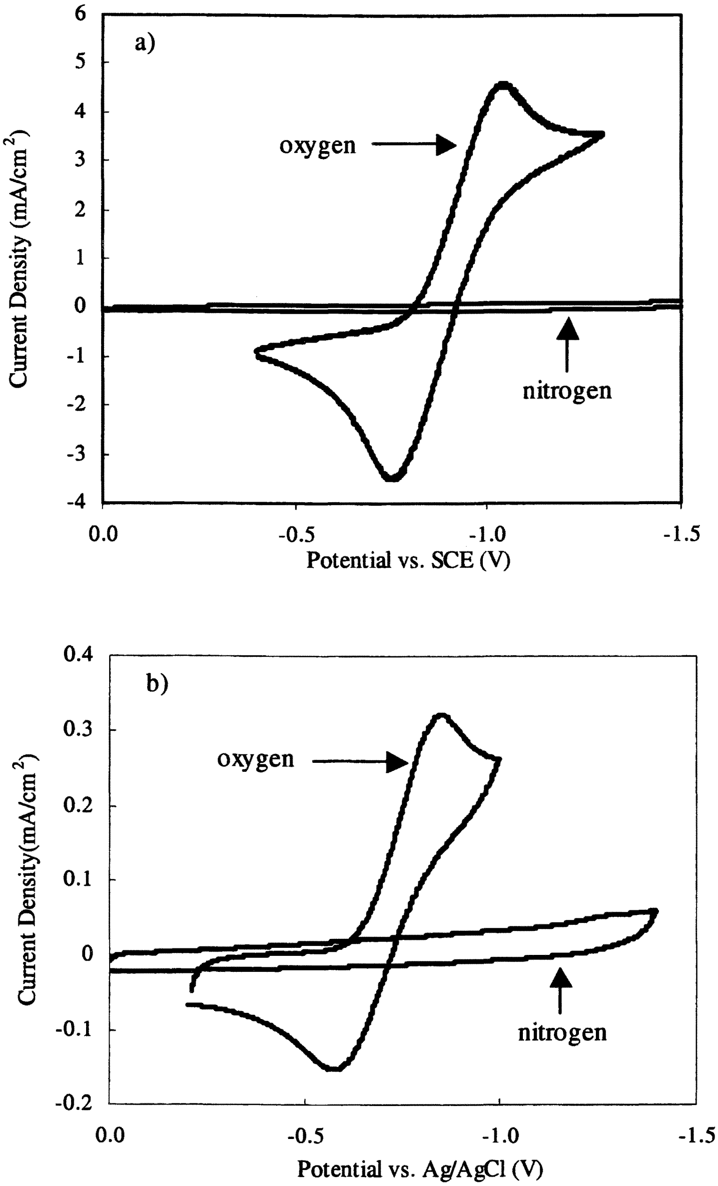

Figure 1 Cyclic voltammograms with nitrogen and oxygen sparging in a) 0.1M TEAP in MeCN and b) BMIM-HFP. All scans used a glassy carbon electrode at a scan rate of 100 mV/s. (Al Nashet et al., "Electro ionic liquids," reproduced by permission of the Electrochemical Society, Inc.)

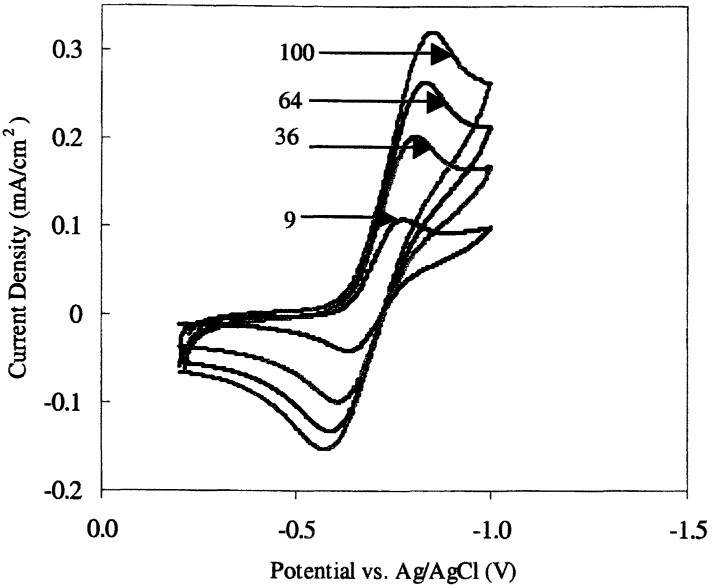

Figure 2 Cyclic voltammograms for various scan rates (mV/s) in BMIM-HFP with oxygen. The working electrode was glassy carbon and the reference electrode Ag/AgCl. (Al Nashet et al., "Electrochemical generation of superoxide in room temperature ionic liquids," reproduced by permission of the Electrochemical Society, Inc.)

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et al. (4) showed that the solvent and electrode materials have significant effect on the reversibility and peak separation of the CVs. The reduction potential for $O_2/O_2^{\bullet-}$ couple shifts to more negative values as the solvating properties of the solvent decrease. The variation in the peak potential for $O_2/O_2^{\bullet-}$ in MeCN and BMIM-HFP is small enough that the peaks seen in the two solvents are consistent with reaction [1]. The scans performed solely in nitrogen showed no such peak. It should be noted that two different scales are used in Figure 1, so the current density for the N_2/MeCN system is approximately the same as that for N_2/BMIM-HFP system. Therefore, the two solvents have comparable electrochemical stability.

It is clear from Figure 1 that the current density for the O_2/MeCN system is much higher, by more than an order of magnitude, than that in the O_2/BMIM-HFP system. This may be due to the difference in the solubility of O_2 in the two solvents. Unfortunately, no data for the solubility of O_2 in BMIM-HFP is available in the literature. Cyclic voltammograms were also run on BMIM-HFP for several scan rates, 9, 16, 25, 36, 49, 64, 81, and 100 mV/s. Four of these are shown in Figure 2. The cathodic peak current is proportional to the square root of the sweep rate, which indicates a diffusion-controlled process. This observation is consistent with reaction [1].

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Conclusions

Preliminary experiments with the RTIL, 1-butyl-3-methylimidazolium hexafluoro-phosphate (BMIM-HFP), showed promise that this solvent was capable of supporting the electrochemical generation of superoxide ion. This finding may lead to new routes for electrochemical oxidation of chlorinated compounds in ionic liquid media.

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Chapter 15

Development of Room-Temperature Ionic Liquids for Applications in Actinide Chemistry

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One area of on-going research in our group at Los Alamos National Laboratory is directed toward characterization of the basic coordination chemistry and electrochemical behavior of f-element ions dissolved in room temperature ionic liquids (RTILs). The ultimate goal of this work is to introduce advanced, environmentally sustainable, nuclear processing and purification strategies into both the DOE complex and the civilian nuclear industry. Efforts to develop ambient temperature electrorefining and/or electrowinning technologies are focused on the design of ionic liquids characterized by extended cathodic stability. In this chapter a summary of the synthesis, physical properties and electrochemical behavior of the ionic liquids used in this work is presented. The feasibility of efficient electrochemical production of highly electropositive metals is demonstrated through reversible plating and stripping of sodium and potassium metals.

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Introduction

The application of room temperature ionic liquids (RTILs) as rationally designed solvent systems to solve chemical and materials science problems is currently attracting a great deal of interest *(1)*. Ionic liquids are low melting organic salts that offer a unique combination of physical properties that can be exploited to develop advanced, environmentally sustainable, chemical technologies. These systems are being actively considered in the development of clean technologies in chemical synthesis, catalysis, electrochemical production of pure metals and alloys, and in chemical separations. A general program has been initiated at Los Alamos National Laboratory to characterize the basic coordination chemistry and electrochemical properties of lanthanide and actinide ions dissolved in RTILs. The goal of this work is to develop advanced, environmentally sustainable, nuclear processing and purification technologies to be implemented within both the DOE complex and the civilian nuclear industry.

Current state of the art in routine actinide recovery and purification can be divided into two main categories: 1) aqueous processing based on PUREX or similar extraction technologies, and 2) electrochemical pyro-refining of metals from high temperature molten salt media *(2)*. In the first category, efficient actinide purification is built upon detailed understanding of the coordination chemistry, hydrolytic behavior, and valence state control of f-element ions and complexes dissolved in aqueous solutions. In the second case, high temperature molten salt electrorefining is used to produce pure actinide metals because of the highly electropositive nature of the metallic f-elements. The actinide metals generally react rapidly and in some cases violently with water to evolve hydrogen and give metal oxides. In order to obtain the pure metals, anhydrous molten salt processes have been developed, which closely resembles the high temperature electrochemical techniques used to produce aluminum metal. Alternative approaches based on RTILs could help solve several long-standing concerns with current technology including nonproliferation issues, criticality safety, equipment degradation, and lack of process flexibility.

Room temperature ionic liquids are fascinating solvents to consider in actinide electrorefining. Development of an RTIL based process to produce pure actinide metals is an attractive possibility. The lower operating temperatures and less corrosive RTIL environment promise reduced production costs. Spent reaction mixtures/solvent systems could be integrated with ion-exchange chromatographic techniques to allow simple recycle schemes that minimize waste. Furthermore, compared to high temperature molten salt conditions, ambient temperature electrochemical processes can be more easily integrated with real-time spectroscopic analysis to allow fine control over reaction conditions and processing parameters. From a safety standpoint the ionic liquids are attractive because they are non-flammable and have essentially no vapor pressure at ambient temperatures. Criticality safety in ionic liquids is also much improved over aqueous solvent systems *(3)*.

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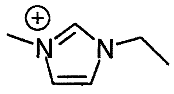
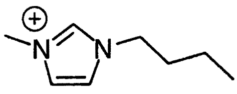
The actinides, aside from being notoriously radioactive, are also among the most electropositive elements. The standard reduction potential of thorium, uranium, neptunium, plutonium, and americium are all more negative than aluminum. The reduction potential of trivalent americium compares most closely to that of magnesium. However, the most well-developed and extensively utilized ionic liquids based on 1,3-dialkylimidazolium cations are incompatible with electrochemical actinide reduction. In order for RTILs to be of general utility in actinide electrorefining/electrowinning, the cathodic stability of the solvent must be extended beyond the limits of 1,3-dialkylimidazolium salts (*c.f.* EMI or BMI). Any attempt to reduce f-element ions to pure metals or alloys in these media would irreversibly decompose the ionic liquid solvent through reduction of the imidazolium ring. In this chapter we summarize our work toward development of RTIL systems characterized by extended cathodic stability. Low viscosity, high conductivity ionic liquids are described and their electrochemical windows are demonstrated. Details of the chemical and electrochemical behavior of actinide ions dissolved in these solvent systems will be reported elsewhere.



EMI



BMI

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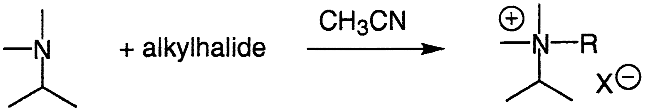
Synthesis and Physical Properties of Ionic Liquids

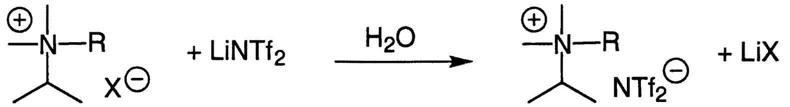
The physical properties of ionic liquid solvents, such as melting point, density, viscosity, conductivity, and polarity depend upon the chemical structure of both the anion and cation. Detailed studies of 1,3-dialkylimidazolium salts combined with a variety of different anions have shown that bis(trifluoromethanesulfonyl)amide, $^{-}N(SO_2CF_3)_2$ ($^{-}NTf_2$), gives air and water stable materials generally characterized by the lowest melting points, lowest viscosities, and highest conductivities of currently available ionic liquids *(4)*. These properties, combined with excellent thermal and electrochemical stability, advocates their use in further ionic liquid development and are exclusively considered in this work.

Ionic liquids characterized by extended cathodic stability can be prepared using quaternary ammonium cations. The viscosity of these systems depends markedly on the molecular weight/molecular volume of the cation. For example, while $[N(Et)_3(n\text{-hex})]NTf_2$ and $[N(butyl)_3(n\text{-hex})]NTf_2$ are each ambient temperature liquids, their viscosity is unacceptable for convenient use as a free flowing solvent (viscosity equals 167 and 595 cP, respectively) *(5)*. It should be emphasized that solvent viscosity is an important property to minimize because rate of solute dissolution, reaction kinetics, ease of handling, and electrical conductivity can all be optimized using low viscosity ionic liquids. For comparison, the lowest viscosity of currently reported ionic liquids is 34 cP (25 °C) for [1,3-ethylmethylimidazolium]NTf_2 ([EMI]NTf_2), which is only slightly greater than the viscosity of ethylene glycol. These values can be further placed into perspective by recognizing that water has a viscosity of only *ca.* 1.0 cP at ambient temperature.

To address this issue, smaller quaternary ammonium salts have been prepared. A series of [NMe_2(*i*-Pr)(R)]NTf_2 salts have been synthesized and their properties correlated with the alkyl group, R (R = Me, Et, *n*-Pr, *n*-butyl, *n*-pentyl, and *n*-hexyl) *(6)*. A simple aqueous metathesis reaction between a quaternary ammonium halide and commercially available $LiNTf_2$ gives the corresponding hydrophobic ammonium $^-NTf_2$ salt, which generally forms a second liquid layer below the aqueous phase (eqn. 1 and 2). A common work-up

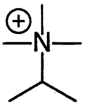


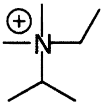
(1)

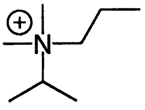


(2)

is followed for all the ionic liquids described in this work. Simply decanting the water and repeated extraction with additional aliquots of water removes lithium halide from the crude ionic liquid. The ionic liquids are then dried under vacuum for at least 48 hours, then passed through a column of dry activated alumina to yield colorless, analytically pure, anhydrous solvents. The highest symmetry ammonium salt of the series, [NMe_3(*i*-Pr)]NTf_2, is obtained as a typical ionic


Methyl


Ethyl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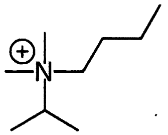
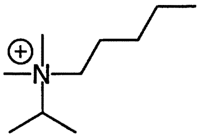
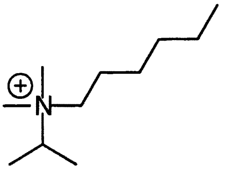

Butyl


Pentyl


Hexyl

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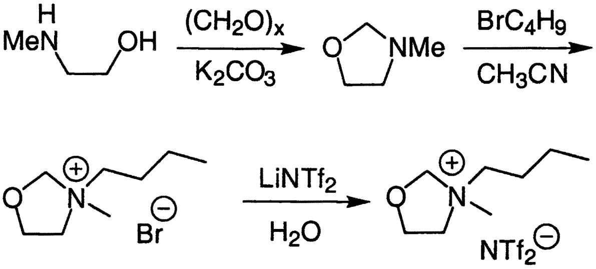
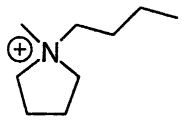
solid (mp = 150 °C) and is isolated by filtration and washed with water. Reduction of the cation symmetry by exchange of one methyl group for an ethyl group (i.e. $[NMe_2(Et)(i\text{-}Pr)]NTf_2$), again gives an ionic solid, although the melting point is reduced to 56 °C. When the variable group, R reaches *n*-propyl or larger, ambient temperature ionic liquids are obtained, in which the viscosity gradually increases across the series (*vide infra*).

A promising ionic liquid design strategy has recently been introduced by MacFarlane and co-workers *(7)*. Incorporation of a quaternary nitrogen center into a five-member cyclic structure gives ionic liquids of considerably reduced viscosity compared to acyclic ammonium salts of similar molecular weight. A nice example is illustrated by [N,N-butylmethylpyrrolidinium]NTf_2 ([BMP]NTf_2). When measured at 30 °C, the viscosity of [BMP]NTf_2 is found to be 60 cP, compared to an acyclic ammonium salt of similar molecular weight, $[NMe_2(i\text{-}Pr)(n\text{-}butyl)]NTf_2$, which is characterized by a viscosity of 103 cP.

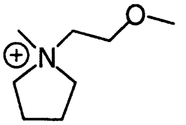


(3)

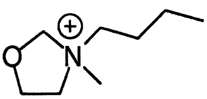
We have prepared the corresponding [N,N-butylmethyloxazolium]NTf_2 ([BMO]NTf_2) ionic liquid to evaluate the effect of oxygen incorporation into the five-member ring (eqn 3). The viscosity of [BMO]NTf_2 (vis = 108 cp, 30 °C) is found to be considerably larger than [BMP]NTf_2. A similar trend is observed for the corresponding six-member ring cations. Thus, [N,N-butylmethyl-



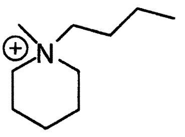
BMP



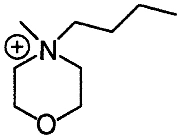
MOMP



BMO



BMPP



BMM

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piperdinium]NTf$_2$ ([BMPP]NTf$_2$) is isolated as a relatively viscous liquid while the related [N,N-butylmethylmorpholinium]NTf$_2$ ([BMM]NTf$_2$) salt occurs as a low melting (mp = 34 °C) solid. Curiously, we find that substitution of the butyl group in [BMP]NTf$_2$ with methyoxyethyl- significantly reduces the viscosity of the resulting [N,N-(methoxyethyl)methylpyrrolidinium] salt (MOMP; vis = 42 cP, 30 °C). In fact, this salt is characterized by one of the lowest viscosities of any non-imidazolium based ionic liquid. The viscosity and conductance of some of these ionic liquids are summarized in Figure 1.

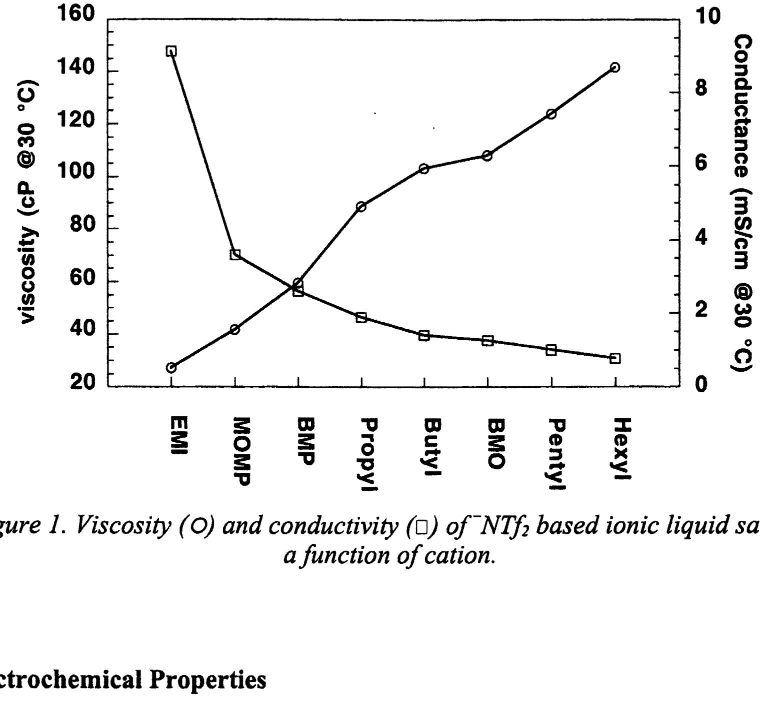

Figure 1. Viscosity (O) and conductivity (□) of $^-$NTf$_2$ based ionic liquid salts as a function of cation.

Electrochemical Properties

Cyclic voltammograms depicting the electrochemical solvent windows of [EMI]NTf$_2$ and [NMe$_2$(*i*-Pr)(*n*-Pr)]NTf$_2$ are compared in Figure 2. The data shown for [NMe$_2$(*i*-Pr)(*n*-Pr)]NTf$_2$ is typical of both cyclic and acyclic quaternary ammonium based ionic liquids. While the cathodic limit is reached for [EMI]NTf$_2$ just before -2.0 V, this limit is extended to *ca.* -3.1 V for the quaternary ammonium salts. The anodic limit, most likely defined by oxidation of the $^-$NTf$_2$ anion, is observed near 3.0 V. The slight variation in anodic limit between [EMI]$^+$ and [NR$_4$]$^+$ salts is a real effect and is attributed to differences in ion-pairing between $^-$NTf$_2$ and the respective cations. These data indicate an effective working electrochemical window for [NR$_4$]NTf$_2$ ionic liquids of just greater than 5.5 V.

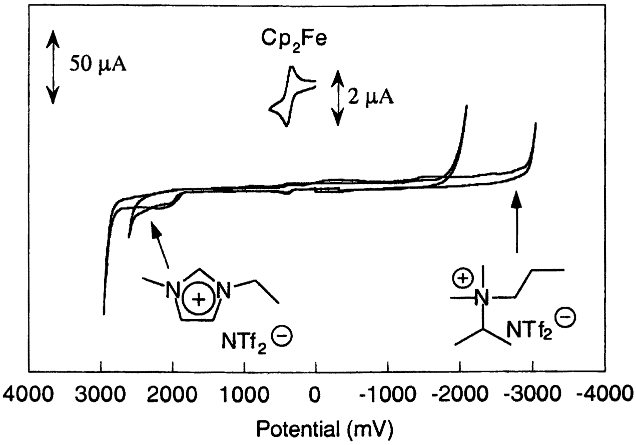

Figure 2. Cyclic voltammograms (CV) of [EMI]NTf$_2$ and [NMe$_2$(i-Pr)(n-Pr)]NTf$_2$ showing solvent limits at 25 °C (Pt working electrode, Ag/AgOTf reference electrode).

The cathodic boundary of [NR$_4$]NTf$_2$ salts have been further tested by examining the electrochemical behavior of highly electropositive sodium and potassium salts. For example, to a suspension of KH in the ionic liquid was added HNTf$_2$, which rapidly evolves hydrogen and forms a homogeneous solution of KNTf$_2$. A cyclic voltammogram of this solution is shown in Figure 3. Sweeping the potential negative gives a rapid rise in current at *ca.* -3.0 V due to plating of potassium metal on the cathode. Reversal of the potential sweep gives a distinctive stripping wave as electrodeposited potassium metal is oxidized from the platinum working electrode. A similar cyclic voltammogram was recorded for NaNTf$_2$ in which plating is observed at *ca.* –2.5 V.

To put this observation into perspective, the standard reduction potentials (aqueous) calculated for Na^+/Na^0 and K^+/K^0 are –2.714 and –2.924 V, repectively. The standard reduction potential calculated for Pu^{3+}/Pu^0, the most technologically important actinide element, is only –2.07 V. In fact all of the standard reduction potentials calculated for the An^{3+} ions are less negative than Na^+/Na^0. This analysis suggests that from a thermodynamic perspective, the electroplating of f-element ions should be readily achieved in these ionic liquid solvents. However, the actual coordination chemistry of the f-element ions dissolved in RTILs should play a fundamental role in the electroreduction process. Strongly coordinated counter ions such as chloride may kinetically inhibit the multi-electron reduction reaction, causing a distinctive over-potential. In the following section, the potential coordination chemistry of simple, formally "bare" metal ions, dissolved in $^-$NTf$_2$ based ionic liquids is considered.

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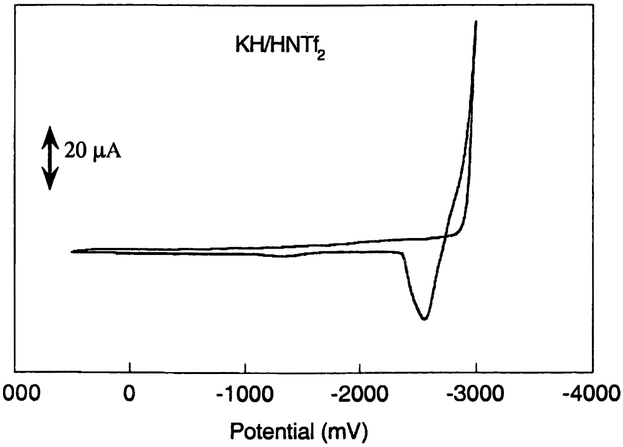
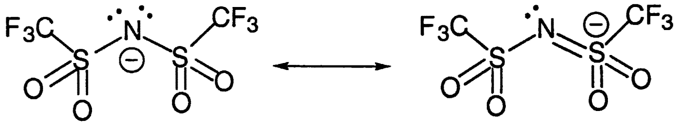


Figure 3. Electroplating and stripping of KNTf$_2$ dissolved in [NMe$_2$(i-Pr)(n-Pr)]NTf$_2$ (Pt working electrode, Ag/AgOTf reference electrode).

Structure and Coordination Chemistry of $^-$NTf$_2$ Based Ionic Liquids

The coordination chemistry anticipated for the ionic liquids under investigation in this work are related to the electronic structure of $^-$NTf$_2$. Single crystal X-ray diffraction experiments carried out for [NMe$_3$(*i*-Pr)]NTf$_2$ (mp = 150 °C) reveal short S–O and N–S bond lengths most consistent with resonance structure **2** (eq 4). Golding and coworkers recently reported the structure of



1 2

(4)

[1,2,3-benzylmethylethylimidazolium]NTf$_2$ and reached a similar conclusion *(8)*. Delocalization of negative charge within the S–N–S core can account for the weak coulombic attraction between the $^-$NTf$_2$ anion and weakly Lewis acidic organic cations (*i.e.* low lattice energy and low melting points).

Although little interaction between $^-$NTf$_2$ and weak Lewis acids is indicated by structural studies of organic $^-$NTf$_2$ salts, the potential of bonding interaction with Lewis acidic metal ions should be considered. Strauss and coworkers employed $^-$NTf$_2$ as a weakly coordinating anion in the study of nonclassical metal-carbonyl complexes. A crystal structure of an $^-$NTf$_2$ anion coordinated to

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a copper (I) atom has been reported *(9)*. In this case, metrical data obtained for $Cu(CO)_2(NTf_2)$ demonstrates that the S–N–S unit becomes slightly modified upon coordination. The S–N–S angle is found to become more acute in the complex (121.9°) compared to $[NMe_3(i\text{-}Pr)]NTf_2$ (124.5°). The S–N bond length also relaxes to *ca.* 1.630 Å compared to 1.575 Å in the uncoordinated anion. These data indicate that resonance structure **1** (eq 4) becomes comparably more important in the metal complex. In this study the donor ability of $^-NTf_2$ was determined to be weaker than the triflate anion, $^-OSO_2CF_3$, but stronger than $[AsF_6]^-$ through comparison of the ν(CO) stretching frequencies measured for $Cu(CO)_2X$ (X = $^-OSO_2CF_3$, $^-NTf_2$, and $[AsF_6]^-$). These data suggest that $^-NTf_2$ based ionic liquids will behave as moderate donor solvents.

In order to obtain a better measure of coordinating ability of $^-NTf_2$ based ionic liquids, we have recently developed a simple spectroscopic probe to estimate the solvent Gutmann Donor Number (DN) *(10)*. The benzylic ^{19}F NMR chemical shift of perfluorobenzyliodide $[ICF_2(C_6F_5)]$ is found to be linearly dependent upon the DN of the solvent in which the probe is dissolved (see Figure 4). The observed variation in ^{19}F chemical shift arises due to weak donor-acceptor interactions between the probe molecule (Lewis acid) and the solvent (Lewis base). By subsequently measuring the benzylic ^{19}F NMR chemical shift of $ICF_2C_6F_5$ dissolved in representative $^-NTf_2$ based ionic liquids, the DN of these solvents can be estimated at *ca.* 10 ± 1. A DN of *ca.* 10 is analogous to the coordinating ability of benzonitrile (NCPh). These ionic liquids should be more strongly coordinating than solvents such as nitromethane (DN = 2.7) or

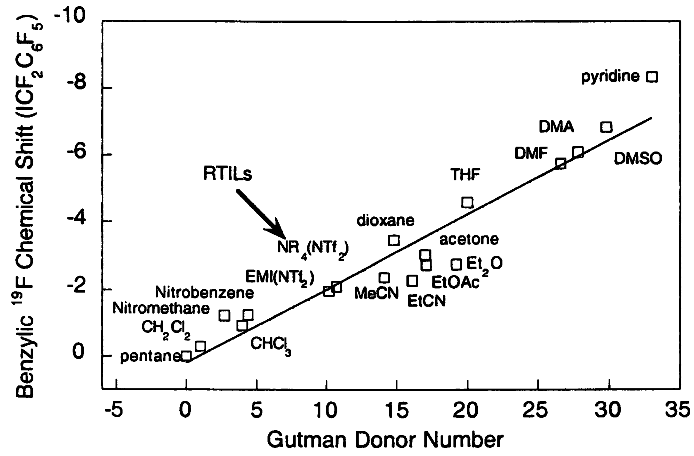

Figure 4. Benzylic ^{19}F NMR chemical shift of $ICF_2C_6F_5$ versus Gutmann Donor Number for several common organic solvents as well as $[EMI]NTf_2$ and $[NMe_2(i\text{-}Pr)(n\text{-}Pr)]NTf_2$.

chloroform (DN = 4), but will be weaker donor solvents than acetonitrile (DN = 14.1) or acetone (DN = 17) *(11)*.

Recent studies by the groups of Seddon *(12)*, Brennecke *(13)*, and Gordon *(14)* have considered the polarity of room temperature ionic liquids as determined using a variety of solvatochromic dyes as spectroscopic probes. Gordon and coworkers correctly point out that most probe molecules allow examination of only one major type of interaction with a solvent (either Lewis acidity or Lewis basicity). The results of Seddon and Brennecke address only the Lewis acidity or Acceptor Number (AN) of the ionic liquids under investigation. In addition to characterization of Lewis acidity, Gordon and coworkers utilized a solvatochromic copper complex, $[Cu(acac)(tmem)]BPh_4$ (acac = acetylacetonate, tmem = tetramethylethylenediamine) to determine the relative Lewis basicity (related to Donor Number) of several ionic liquids composed of imidazolium cations and several different anions ($^-PF_6$, $^-BF_4$, $^-NTf_2$, and ^-OTf). This copper complex was previously used to determine DNs of anions dissolved in common organic solvents suggesting its suitability as a probe of ionic liquid basicity *(15)*. The Lewis basicity of the ionic liquids was found to depend exclusively upon the anion. The relative basicity of the series predicted by this study is $^-PF_6 < {}^-BF_4 < {}^-NTf_2 < {}^-OTf$, consistent with the work of Strauss and coworkers. An absolute measure of DN was not assigned, pending further investigation.

Conclusions

Room temperature ionic liquids composed of either acyclic or cyclic quaternary ammonium cations combined with the $^-N(SO_2CF_3)_2$ anion have been evaluated for potential applications in actinide electroprocessing. This particular class of ionic liquids was found to combine favorable viscosity and conductivity properties with excellent electrochemical stability. Cathodic stability was demonstrated in this work through the reversible plating and stripping of highly active sodium and potassium metals, suggesting their use in f-element electroplating. Bis(trifluoromethylsulfonyl)amide based ionic liquids are expected to behave as moderately coordinating solvents comparable to benzonitrile. The coordination chemistry and electrochemical behavior of lanthanide and actinide metal ions dissolved in this medium are the subject of continued investigation.

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Chapter 16

Ionic Liquids and Metal Ions: From Green Chemistry to Ore Refining

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Reactions in ionic liquids for a range of applications involving metal ions and their compounds are described. Applications in organic synthesis are exemplified using organostannanes in environmentally friendly allylation reactions, and metal-directed macrocycle formation via Mannich-type reactions. In addition, applications in metal recovery are introduced, namely oxidative leaching of chalcopyrite ore and copper electrodeposition in the presence of ionic liquids.

Chemistry in molten inorganic salts has a venerable history and is still of importance to us (*1*); for example, the manufacture of aluminium is centred on electrodeposition in an ionic melt (*2*). However, the complexities of working at high temperatures make developments of molten ionic salt chemistry difficult and, given the temperatures necessary to achieve a melt in many cases, prohibit use of the molten salts for almost anything but reactions involving inorganic systems. The development of ionic species that are typically a mixture of an organic cation and an inorganic anion, and are liquid at or near room temperature, has opened up new opportunities in synthesis (*3*), by allowing the opportunity to perform reactions in an ionic environment at lower temperatures.

In Ionic Liquids; Rogers, R., et al.;
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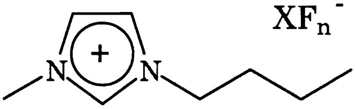
These ionic liquids incorporating an organic cation present properties that are immediately attractive. They are reasonably robust and benign materials that are liquid over a wide temperature range without undergoing decomposition, exhibit essentially no vapour pressure, are miscible with a range of solvents including in some cases water, and will dissolve a wide range of compounds from simple organic molecules to metal salts, often to high concentration (*4, 5*). However, they are not simply innocent solvents. Their ionic nature can influence reactions that occur in them through displacement of equilibria and alteration of transition states and activation barriers. An obvious consequence of this is that reaction outcomes may be altered, particularly compared with the same reaction performed in solvents of low polarity. However, product profiles may not differ all that much from those in highly polar solvents. What will change, importantly, is the capacity to work over an extended range of temperatures.

As a result of their properties, ionic liquids have developed recently as key reagents for so-called green chemistry. This forms part of the drive towards ‘clean technology’; as manufacturers work towards zero waste and emissions from plants, new technologies need to develop to serve these goals. A key feature of ionic liquids that makes them attractive is their capacity to be reused in reactions with limited and often facile cleaning. This is environmentally appropriate, while reuse also reduces costs significantly.

It has been known for some time that many simple metal ion salts and organometallic compounds dissolve to high concentrations in ionic liquids. Thus, solution chemistry involving metal ions and their compounds is clearly possible in ionic liquids. Despite their potential, however, interest in their applications has been curiously limited. Their potential in solvent extraction processes has been recognised and probed (*6, 7*), but otherwise applications have been little explored. In this chapter we present examples of reactions in ionic liquids involving metal ions, including potential applications in metallurgy. In particular, we will focus on reactions using the established ionic liquid featuring the 1-butyl-3-methylimidazolium cation ([bmim]) as either its tetrafluoroborate or hexafluorophosphate salt.



(X = B, n = 4 or X = P, n = 6)

Reactions Involving Organometallic Compounds

Organometallic compounds are obvious candidates for reactions in ionic liquids, since their composition and polar or even ionic character usually makes

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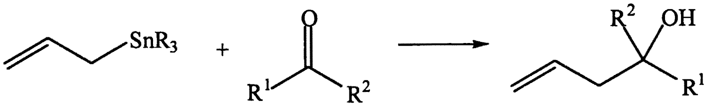
them soluble and hence readily available for reactions. Moreover, the ionic nature of the solvent may assist in stabilising certain transition states, with presumably at least ionic transition states favoured as a result of strong ion-pairing interactions (*8*). This is consistent with ionic liquids behaving as not purely innocent solvents, but, like solvents generally, playing a role in influencing the chemistry conducted in their matrix. Their use in synthesis has been reasonably well examined for a range of organic reactions (*9*), but to date reported examples in organometallic chemistry have been more limited but are growing rapidly (*4*). Organometallic reactions in ionic liquids offer the opportunity to conduct chemistry in an environmentally benign solvent that can also be recycled, rather than the traditional molecular organic solvents. Provided high-yielding reactions with high atom efficiency can be achieved, the benefits of this reaction medium are apparent. Further, there is the prospect of reactions proceeding with more appropriate regio- or stereospecificity, which may make outcomes even more attractive.

Reactions with Organostannanes

Organometallic compounds find application in a range of organic syntheses. For example, the addition of allylic metal compounds to ketones and aldehydes produces homoallylic alcohols. This transformation is useful in organic synthesis and hence has attracted continuing attention recently (*10*), aided by enhanced versatility through the ability to introduce a variety of functional groups by manipulating the alkene moiety. In particular, allylation of aldehydes with allylic stannanes had proved attractive due to a good balance of configurational stability and reactivity (*11*). Recently, it has been noted that the reaction of tetraallylstannate with aldehydes (eq 1) is significantly affected by choice of solvent, with high yields observed in methanol and other polar solvents (*12, 13*). Since a solvent stabilised ion-pair has been proposed to be involved, it seemed likely that reaction in a pure ionic liquid may influence the transition state and hence the reaction outcomes.

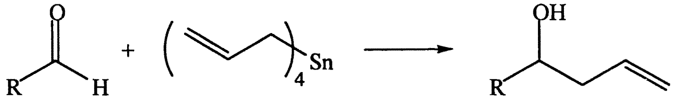


(1)

Allylation Reactions

Although the reaction of allyltrimethylstannane with aldehydes is promoted by methanol, it still occurs at too slow a rate to be of practical use. However, the tetraallylstannane reacts much faster, with allylation reactions sometimes completed in several hours at room temperature (*12*). The reaction is also highly chemoselective, as observed by the high level of discrimination favouring aldehydes over ketones. A mechanism featuring directed hydrogen bonding between the carbonyl compound and methanol has been proposed recently (*12*), although prior work in polar organic solvents favoured ion-pairing of an ionized intermediate (*14*). With the [bmim](XF_n) ionic liquids as solvent, the opportunity for strong hydrogen bonding is remote as only C-H groups are present in the solvent, but an ion-pairing mechanism could be easily supported, suggesting that reaction should proceed in such a solvent environment.

Reaction as outlined in eq 2 was pursued for a range of aldehydes including alkyl, alkene and aromatic forms at ~15°C for 16 h in either 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) or its hexafluorophosphate analogue ([bmim][PF_6]) (*15*). For aromatic aldehydes including those with electron-withdrawing substituents, yields obtained ranged up to 93%. Weak electron-donating substituents did not hinder the reaction, although when a strong electron-donating group (such as Me_2N) was present the reaction did not proceed, mirroring a similar observation for reaction in methanol. Recycling of the ionic liquid was achieved with a simple washing protocol, involving dissolving the ionic liquid in ethyl acetate, washing with water and brine, and adding diethyl ether to separate essentially pure ionic liquid from the mixture of other solvents. Reaction yields showed that repeated use of recycled ionic liquid did not affect yields to any measurable extent, even after several cycles. Establishing reuse protocols is important for use of relatively expensive ionic liquids, and, significantly, this study has clearly defined that reuse need not affect product yields at all.



(2)

Some comparative yields in different solvents appear in Table I, although it should be noted that reaction conditions employed were slightly milder for ionic liquids (15°C, 16h) than in other solvents (30°C, 20 h). What is nevertheless clear from this study is that little difference was found in the yields obtained using methanol, [bmim][BF_4] or [bmim][PF_6] as solvent. Although reactions with aliphatic substituents appear less successful in ionic liquids, the presence of initial reactants in the final reaction mixture in those cases suggest the reactions have simply not gone to completion in the timeframe employed. Generally, solvents capable of hydrogen or ionic bonding are effective, whereas non-hydrogen bonding solvents like dichloromethane are not efficient solvents. This supports an ionic or strongly hydrogen bonded transition state, although the exact mechanism has not been clearly elucidated as yet.

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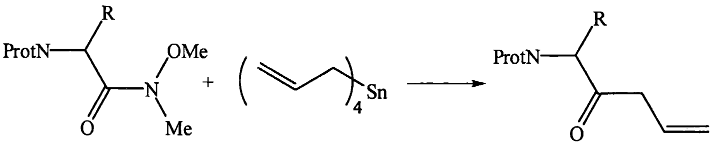
Table I. Yields of homoallylic alcohols from RCHO in various solvents

R-group	*Solvent*	*% yield*
i-Propyl	methanol	84
	dichloromethane	<5
	[bmim][PF_6]	70
	[bmim][BF_4]	70
Phenyl	methanol	81
	formamide	84
	[bmim][PF_6]	82 (83)[a]
	[bmim][BF_4]	79 (78)[a]

(a) Result obtained using recycled ionic liquid after third cycle

A 'Green' Route to N-protected Allylic Alcohols and Ketones

The basic chemistry explored above has been extended further by applying it to the development of a simple 'green' route to *N*-protected homoallylic alcohols and allyl ketones (*16*). Weinreb amides with *N*-phthalimido and *N*-benzyl protection react readily with tetraallylstannane in both methanol and [bmim][BF_4] according to eq 3.



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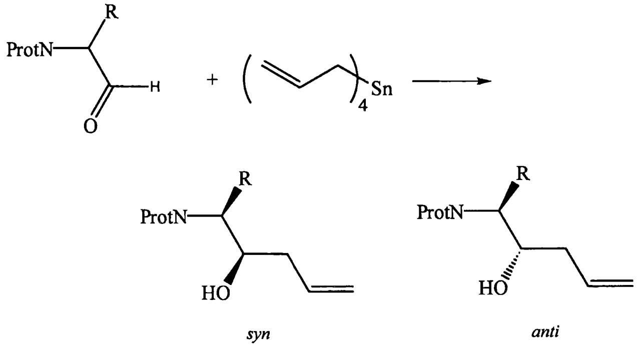

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The reaction involves refluxing in methanol for 5 days, or reaction in the ionic liquid at a similar temperature for the same time. Yields in the ionic liquid ranged from 33 – 56%, following facile direct extraction of products from the ionic liquids with diethyl ether. Milder conditions (30°C, 24 h) with the more reactive *N*-protected aminoaldehydes yielded a mixture (eq 4) of *syn* and *anti* products, with overall yields of 45 – 82%. The *syn* isomer is favoured, but diastereoselectivity proved essentially identical in the ionic liquid and methanol. Varying the protecting group from phthalamido to benzyl also had little effect, with the R-group of the parent amino acid most responsible for variation in *syn:anti* ratio. The reaction in [bmim][BF_4] proved simpler and yielded a modest improvement in diasterioselectivity compared with the earlier reaction in a high-pressure reactor (*17*). Recycling of the ionic liquid is also practicable in this case.

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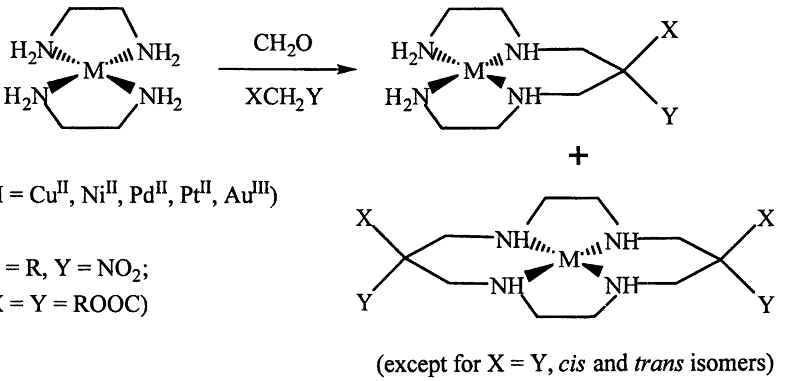
Metal-Directed Macrocyclisation Reactions

The use of metal ions as templates to direct the formation of macrocyles containing heteroatoms and carrying pendant groups, and acyclic analogues, has been explored in detail in recent decades (*18*). Where Mannich-type condensations involving formaldehyde and a carbon acid are concerned, reactions are often possible in aqueous as well as non-aqueous environments. A typical reaction is shown in Figure 1 (*19*) for ethane-1,2-diamine, with the presence of the metal ion reducing the synthesis to formation of new, small chelate rings, which favours their formation.



(M = Cu^{II}, Ni^{II}, Pd^{II}, Pt^{II}, Au^{III})

(X = R, Y = NO_2;
X = Y = ROOC)

(except for X = Y, *cis* and *trans* isomers)

Figure 1. Reaction products for square-planar metal-directed Mannich type reaction of ethane-1,2-diamine forming acyclic and cyclic products

However, hydrolysis reactions leading to metal hydroxides can compete, and particularly with larger-chain diamines (such as propane-1,3-diamine or larger), the yield of macrocycle can be very low, if it forms at all (*20*). This can

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be corrected by using less labile, but expensive, metal ions such as palladium(II). For economic reasons, use of an inexpensive metal ion like copper(II) is favoured provided an appropriate route to larger rings can be established.

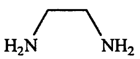
Further, the metal-directed reaction has proven to be highly sensitive to the presence of substitutents on the diamine precursor. Progressive introduction of methyl groups alone leads to a variation in the yield of macrocyclic compared to acyclic product (*21*).

We have recently been exploring the use of an ionic liquid in place of alcohol or water as solvent for the Mannich type condensation reaction, described above. Using bis(diamine)copper(II), nitroethane and formaldehyde in basic solution yields results that are summarised in Table II for reactions employing the specific diamines also drawn there. Reactant ratios, reaction times and reaction temperatures were identical for the study in methanol and [bmim][BF_4] reported, allowing a close comparison of the effect of changing from a polar molecular solvent to an ionic liquid. Further, reaction conditions which give, respectively, modest and low yields of acycle and macrocyle (in methanol) were selected for comparison, so as to highlight any variations in the ionic liquid environment.

Table II. Yields for the Mannich Reaction in MeOH *vs* Ionic Liquid (IL)

Precursor Diamine[a]	*Macrocycle (% Yield)*		*Acycle (% Yield)*		*Overall Yield (%)*	
	MeOH	IL	MeOH	IL	MeOH	IL
1	<1	<1	55	71	56	72
2	<1	<1	23	33	24	34
3	~1	~5	62	88	63	93

(a) Diamines used are drawn below:



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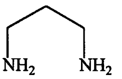

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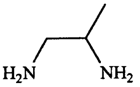

(3)

It is clear that the copper(II)-directed Mannich reactions in the ionic liquid yield similar outcomes from reaction in methanol, although yields are clearly enhanced and 'cleaner' in the ionic liquid, with fewer by-products observed. The step from a polar protic solvent to a non-protic purely ionic medium is sufficient to influence reactant solvation or ion pairing for both ground state and transition states. In this case, both overall yields and ratio of acyclic to cyclic products vary with solvent, at least using identical reaction times. It is possible that a polyimine intermediate, arising from the initial amine-formaldehyde condensation that occurs prior to participation of the carbon anion in cyclisation, is stabilised in [bmim][BF_4]. Yields may also be influenced by the acidity of the carbon acid in the medium, since the carbon anion is a key reactive intermediate; the acidity may differ markedly in the ionic liquid compared with methanol. Given the similarities in the allylation reactions in methanol and ionic liquid, similar behaviour in this case is not surprising. More extensive investigations of ionic liquids in metal-directed organic reactions are proceeding.

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Applications in Metal Recovery

Recovery of metals from ores, concentrates and mattes is a major industry worldwide. As high quality ore bodies are progressively mined out, ores will need to be sourced from less rich and or more geologically complex sites, which places demands on current technologies for recovering metals from the ores. One area that is attracting continuing attention is bioleaching with bacteria such as *Sulfolobus metallicus* (*22*). However, this technology can be slow, limiting in applicable conditions, and is not able to be used for all ores. In a step in a different new direction, we have been exploring a role for ionic liquids in metals recovery. Here, preliminary results involving recovery of copper from chalcopyrite are presented.

Oxidative Leaching

Leaching is the process of dissolution of the economic minerals of an ore or concentrate and generally has been done by an aqueous solution that contains some leaching agent whose role is to enhance the dissolution process (*23*). Ideally, leaching yields a pregnant liquor of the economically important minerals and a residue sufficiently free of metal values for it to be discarded. Leaching has a long history, having been examined for around a century, and is applied in the processing of a number of minerals. Oxidative leaching involves the use of chemicals designed to oxidise usually the anion in an ore or concentrate, thus facilitating the concomitant dissolution of the metal ions present into the leach liquor. For sulfide ores, oxidative leaching is directed towards oxidation of the sulfide ion to sulfur or even to sulfate.

Of the copper sulfide minerals, chalcopyrite is most abundant, but is also most difficult to leach. Use of acid ferric sulfate solution for oxidative leaching chalcopyrite is attractive because of the ease of the following step of electrowinning copper from the resultant acid sulfate solution. However, the leach is particularly particle size dependent and hence energy demanding.

Extraction for 3 hours at ~95°C recovers only 12% of copper from 50 μm particles compared to 90% recovery for 5 μm particles (*24*). Recovery from chloride solution is efficient, but the ferric chloride medium is very corrosive and subsequent electrodeposition from chloride media frequently results in powdery deposits (*25*). Leaching of chalcopyrite has been probed by other means, but there remains no commercial installation that processes this ore by a hydrometallurgical route, perhaps indicative of the challenges extant with this ore. It is these observations that make it a primary target for examination of recovery employing a previously unexplored technology – use of an ionic liquid.

The oxidative leaching process involves oxidation of the sulfide ion to produce usually sulfur, which permits the metal ion to dissolve into the solution. Surface coating of the leaching mineral by sulfur is one factor limiting the success of the leaching of chalcopyrite. There exists the prospect that the sulfur in the presence of ionic liquid will either not be effective in coating particles or else may be removable by distillation from the non-volatile solvent. The prospect of enhanced recovery and more rapid leaching are key attractions.

In this preliminary study, [bmim][BF_4] was used as the ionic liquid and ferric tetrafluorborate as the leaching agent of chalcopyrite of average particle size 100 μm. The chalcopyrite used contained 24% copper, with pyrite (FeS_2) the major impurity. Comparisons were made between aqueous and 1:1 aqueous:ionic liquid environments in the presence or absence of added HBF_4. The primary role of the acid is to stop the formation and subsequent precipitation of iron hydroxide polymers, which may coat particles and may limit dissolution (*26*). In non-aqueous environments, the presence of acid may not be essential, since precipitation of hydroxides will not be a problem.

Extraction of chalcopyrite with $Fe(BF_4)_3$ in aqueous solution alone proved reasonably efficient. For example, a recovery of 50% of the copper was obtained in only a two hour leach at ~100°C compared with 30% recovery from a 1 M HNO_3 leach under comparable conditions. It has been noted that a ferric sulfate leach was not complete even after 80 h (*24*). After 8 hours with ferric tetrafluoroborate in 1:1 water:[bmim][BF_4], an extraction of 90% of available copper was routinely achieved.

A comparison of the %Cu extracted using $Fe(BF_4)_3$ in water and 1:1 water:[bmim][BF_4] over a 4 h period appears in Figure 2 below. It is clear that leaching involving the ionic liquid, even in a solvent mixture, is more rapid than achieved in water alone. Further, overall extraction after more extended periods of time is superior (~15% more) for the ionic liquid solution.

Performing the extraction at ~100°C under vacuum, where water and perhaps sulfur formed in the reaction are removed to a cold trap, leads to an increase in copper dissolution with 45% recovery after only 0.5 h compared with 30% under analogous conditions in the absence of vacuum. Extraction at up to 120°C under vacuum was examined, with greater copper recovery to solution observed, although it was found that mixing needs to be performed reproducibly

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for consistent results to be achieved. There is sufficient evidence from these 'wet' ionic liquid experiments to indicate that use of ionic liquids can promote both rate and extent of copper ion dissolution.

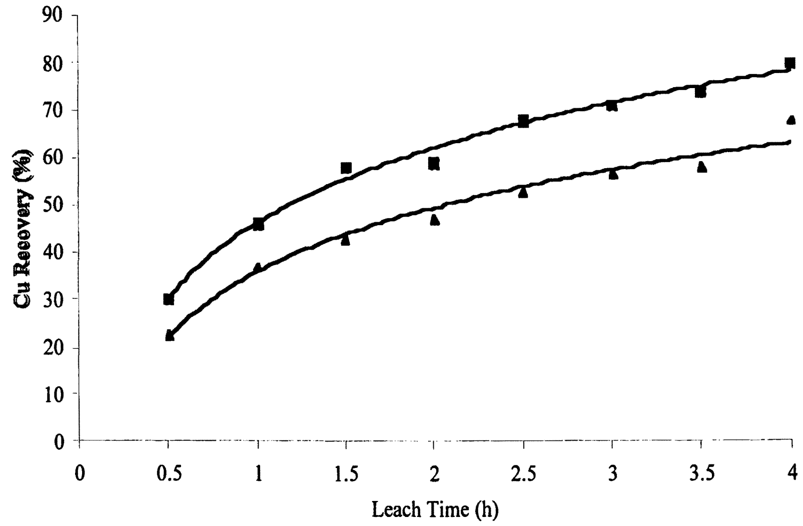

Figure 2. Comparison of copper extraction from chalcopyrite in water (triangles) and a 1:1 ionic liquid:water mixture (squares).

Electrodeposition

An important part of the recovery of copper from its ores is its electrodeposition on the cathode of an electrolytic cell. This is because, regardless of whether the crude copper is isolated by a pyro- or hydro-metallurgical route, electrodeposition is the only viable method to produce copper pure enough for use in electrical applications. The rate of deposition of copper is limited by the maximum current density at which smooth deposits form. If deposits are not reasonably smooth they do not meet market expectations and, in the worst case, dendritic growths can lead to shorting between the closely spaced plates.

In aqueous electrolytes, a number of additives are required to achieve reasonably smooth deposits in commercial cells. The control of dendritic growths by the use of additives involves compounds such as thiourea or else complex mixtures of chemicals including gums. These appear to work either through metal ion complexation in solution influencing redox properties and hence deposition character, or else by physical or chemical adsorption onto the

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surface influencing crystallite nucleation and growth on crystal faces. Despite their presence, the achievement of very high current densities to accelerate throughput in the electrodeposition process has not been forthcoming, and the search for new additives is continuing.

The use of ionic liquids, either as an additive in aqueous solutions or as pure electrolytes, offers attractive possibilities. Potential use of ionic liquids in battery applications attracted attention at an early stage (*27*). There have been recent reports of successful electrodeposition experiments employing chloroaluminate-based ionic liquids (*28*), but these are very hygroscopic and need to be protected from moisture. Here, we have deliberated employed a water-miscible ionic liquid, [bmim][BF_4], as a mixture with water for electrodeposition studies. The ionic liquid in water may behave as a detergent, since it carries a positive head-group and an aliphatic tail. This has the potential to influence solvent properties. Further, and perhaps more importantly, the molecular cations may form an ordered monolayer on the cathode surface, with the cationic heads layered close to the surface and the organic tails pointing out into the solution, producing a hydrophobic layer on the electrode surface. A schematic of this arrangement appears in Figure 3. The inorganic counterions may also contribute to an ordered pattern in the electrical double layer, although in water-ionic liquid mixtures it is apparent that water would also participate. This type of packing would produce an outcome similar to chemisorption of molecules directly to the metal surface, but they would have the advantage of ionic rather than chemical bonding, thus limiting the prospect for their being incorporated into the growing electrode surface as impurities. This would be advantageous for enhanced purity of copper deposits.

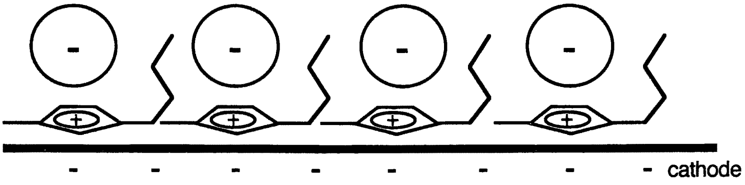

Figure 3. A schematic of a possible ordered structure at the cathode surface.

For current densities above ~400 A/m^2, dendritic growth during copper electrodeposition can be pronounced. Examination of the effect of current density on electrodeposition character is conveniently performed using a Hull cell (*29*) illustrated in Figure 3. The cell has non-parallel cathode and anode, and consequently current density varies along the cathode. The mode of variation is defined, and hence deposition behaviour along the cathode can be related to current density at particular distances. For an applied current of 2 A, current

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densities as high as 1000 A/m^2 and as low as 10 A/m^2 are obtained across the electrode; limits for a 1 A applied current are given on Figure 4. Electrodeposition of copper from tetrafluoroborate solutions was performed with applied currents of 1 – 1.5 A for periods of 2 – 3 h at room temperature.

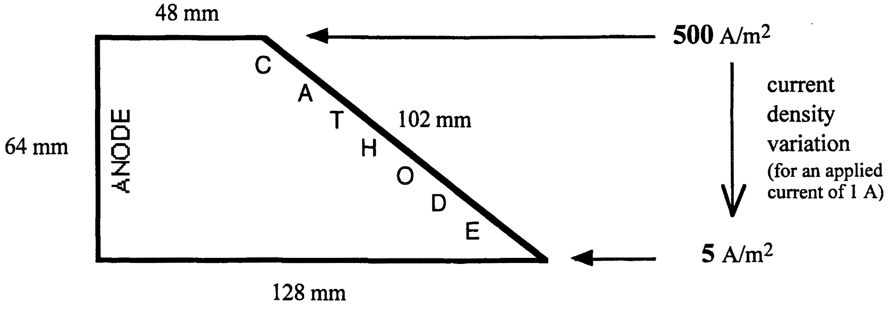

Figure 4. Plan of a Hull cell

With the ionic liquid [bmim][BF_4] added to water, no significant improvement in deposition smoothness was observed at 1% (v/v) addition. However, when 5% [bmim][BF_4] was present, the improvement was significant. Using water alone as solvent produced highly porous and voluminous dendritic copper deposit; in the presence of 5% ionic liquid, a substantially more dense deposit with reduced dendrite formation was observed (Figure 5).

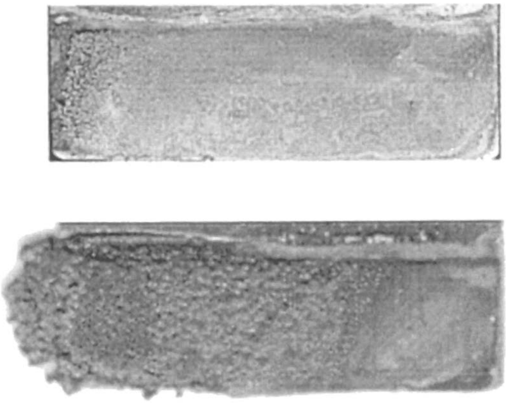

Figure 5. Comparison of electrodeposition of copper from 1 M aqueous $Cu(BF_4)_2$ solution: (top) in the presence of 5% [bmim][BF_4]; (bottom) without any ionic liquid added. (Current density decreases from left to right.)

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It is presumed that sufficient ionic liquid must be present to influence the surface and or solution properties. Because enhancing structures established in the cell in this study must involve ion pairing and not complexation or chemisorption, higher concentrations may be required compared with organic additives such as thiols, where different mechanisms must operate. This may account for a marked improvement only with ~5% loading of ionic liquid. Deposition was subsequently examined at a range of ionic liquid concentrations up to 85%, and in each case successful deposition was achieved with smooth deposits. However, the improvements compared with deposition from 5% ionic liquid solution were not substantial, and current efficiency fell at the high percentages, which does suggest the occurrence of some low level parasitic electrode reaction directly involving either the ionic liquid, or some impurity contained therein. Aspects of this work are under continuing study. However, even at this stage, it seems that ionic liquids offer promise as low concentration additives for electrodeposition, while deposition chemistry in high concentration or pure ionic liquid presents both challenges and opportunities for future study.

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Conclusions

The ionic liquids [bmim][BF_4] and [bmim][PF_6] are versatile solvents for a range of reactions involving metal ions and their compounds. Their benign nature and ability to be successfully recycled is part of their appeal, although their ability to influence product distributions is also a key to future use. The diversity of uses examined in this broad-brush collection of studies is indicative of their potential, although it is clear that they are not inevitably successful reaction matrices. However, their prospective use in industrially significant tasks in the minerals industry, such as leaching and electrodeposition, is one particular area that deserves and is attracting further research.

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Chapter 17

Ionic Liquids in Perspective: The Past with an Eye Toward the Industrial Future

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Molten salts have a long and important history in industrial chemistry, but ionic liquids have found industrial applications more recently. The "modern" history of ionic liquids started with the development of aluminum chloride-based salts for electroplating in 1948. Since then basic research efforts have shown that ionic liquids may be used for batteries, organic synthesis, extractions, and alloy electrodepositions. The most commonly used type of cation in ionic liquids is the 1,3-dialkylimidazolium ion.

Ionic liquids are now considered a special subset of molten salts, generally having temperatures of 25°-100° C in their liquidus range. They are a subset of molten salts, but have properties different enough to merit a distinction. The "modern" history of ionic liquids started with the development of aluminum chloride-based salts for electroplating in 1948. Since then the considerable basic research efforts have shown that ionic liquids may be used for batteries, organic and inorganic synthesis, spectroscopy, extractions, and alloy electrodepositions. The most commonly used type of cation in ionic liquids is the 1,3-dialkylimidazolium ion. The reason for the popularity of this slightly unusual cation is partly scientific and partly historic. The 50-year story of the

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development and uses of the imidazolium-based ionic liquids is an interesting example of multidisciplinary and multinational collaboration and competition.

This paper is not meant in any way to be a comprehensive scientific review of ionic liquids. Instead this is a retrospective on the development of ionic liquids from the perspective of the group at the U. S. Air Force Academy, which has had a continuous research program in molten salts since 1963. During this unusually long research effort on low temperature molten salts the group has had only three principal investigators; Lowell A. King, John S. Wilkes and Richard T. Carlin. Of course, the complete story of ionic liquids goes well beyond those people. Their predecessors in the field, collaborators, colleagues at the Air Force Academy and in the field, and competitors have all combined to make low temperature molten salts an interesting and vital field. The longevity of the research in low melting fused salts at the Air Force Academy and in some other groups in the U. S. is in no small part due to the faithful funding support from the Air Force Office of Scientific Research (AFOSR). Again, just a few program managers at AFOSR have ensured that the research always had a sponsor. They were Denny Elliot, John Wilkes (working at two places for 9 years), Hugh DeLong, and Paul Trulove. Finally, the Electrochemical Society and the Gordon Research Conferences have been important forces in the development of room temperature molten salts as a viable scientific and technolgical field in the U. S. In Europe and Asia this emerging field of neoteric solvents has found a podium in several long-standing conferences dedicated to chemistry and technology of molten salts.

The previous paragraph contains many synonyms used for ionic liquids. "Molten salts" is the most common and most broadly applied term for ionic compounds in the liquid state. Unfortunately the term "ionic liquids" was also used to mean the same thing long before there was much literature on low melting salts. See Inman's book "Ionic Liquids" from 1981(*1*) and Copeland's book "Transport Properties in Ionic Liquids" from 1974 (*2*). It may seem that the difference between ionic liquids and molten salts is just a matter of degree (literally), however the practical differences are sufficient to justify a separately identified niche for the salts that are liquid around room temperature. That is, in practice the ionic liquids usually may be handled like ordinary solvents. There are also some fundamental features of ionic liquids, such as strong ion-ion interactions that are not often seen in higher temperature molten salts.

An important question underlying the topic of this book is why (or why not) would one want to use ionic liquids or molten salts as a medium for chemistry on a small or large scale. It is abundantly clear that molecular liquids dominate chemical processes where solvents are used. This is undoubtedly because there are a large number of molecular liquids with a wide range of chemical and physical properties that are liquid at standard temperature and pressure. Water is the cheapest and most obvious example. Traditional molten salts have very high melting temperatures, such as 800° C for NaCl, and even lower melting eutectics

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like LiCl-KCl (m.p. 355° C) require uncomfortably high tempertures. Considerable heat is needed to maintain the salts as liquids, and materials incompatibilities are a major problem in their use as media for chemistry. Furthermore, the preparation and use of molten salts are unfamiliar to most chemists. Nevertheless, there are some large-scale industrial processes and some useful devices that use molten salts as their medium for the chemistry that makes them work. Examples are the Hall-Héroult process for aluminum production, molten carbonate fuel cells, and thermal batteries. The reasons why molten salts are used are:

- A wide liquidus range
- Low volatility
- Broad stability range (chemical, thermal, electrochemical)

Ionic liquids, as defined here, avoid the principal disadvantage of molten salts (the high temperature) while retaining most of the advantages of liquidus range, volatility and stability. Unfortunately ionic liquids are still unfamiliar to most chemistry practitioners and students.

The history of ionic liquids goes back much further than we thought when we first started searching for a lower temperature replacement for LiCl-KCl in thermal batteries. There are 29 million substances registered with Chemical Abstracts, so it is not surprising that a new matierial you prepare has been made before. The earliest description of materials similar to what we now know as ionic liquids goes back to the 19th century development of Friedel-Crafts chemistry. In these reactions an aromatic compound, like benzene, may be alkylated or acylated by alkyl halides or acyl halides, such as methyl chloride or acetyl chloride. Importantly, the reaction requires a Lewis acid catalyst, the most common being $AlCl_3$. A highly colored separated phase often developed during the reaction, and the material in that phase appeared to participate in the reaction. That phase was called "red oil" and we would now recognize it as a chloroaluminate ionic liquid. It is the chloroaluminate salt of the sigma-complex intermediate in the Friedel-Crafts alkylation, and probably has the composition shown in Figure 1.

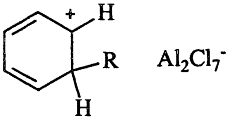

Figure 1. "red oil"

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The true composition is undoubtedly more complicated than this, but in fact this ionic liquid phase has been proposed as an effective catalyst in indusrial alkylation processes(*3*).

Another progenitor of chloroaluminate ionic liquids was the liquid chlorocuprate work of John Yoke at Oregon State University in the early 1960's. Copper(I) chloride (CuCl) and triethylammonium chloride (Et_3NHCl) are both solids, but form a liquid at room temperature when mixed (Eq. 2)(*4*).

$$CuCl(s) + Et_3NHCl(s) \longrightarrow Et_3NHCuCl_2(l) \qquad (2)$$

Reactions among various chlorocuprate ions and chloride are analogous to those known to occur in chloroaluminates. This ionic liquid proved somewhat useful for spectroscopy, but was not widely used for other purposes.

Liquid clathrates were discovered and extensively studied by Jerry Atwood and coworkers at the University of Alabama in the 1970's, and bear a general resemblance to chloroaluminate ionic liquids. These remarkable materials are composed of a salt combined with an aluminum alkyl, which then forms a compound with one or more aromatic molecules(*5*). A formula for the ionic portion is $M[Al_2(CH_3)_6X]$. The anion in the salt MX forms an Al-X-Al bridged anion with the trimethylaluminum, which then forms an inclusion compound with an aromatic guest as the temperature is raised (Eq 3). While these liquid clathrates are not strictly ionic liquids due to the aromatic molecules, they have been patented for use in coal liquefaction and petroleum recovery from tar sands(*6*). The liquid clathrates discovered by Prof. Atwood have an interesting but indirect connection to modern-day ionic liquids. Four of Atwood's students at the University of Alabama were Robin Rogers, Richard Carlin, Michael Zaworotko, and Joan Fuller. These names will appear later in the saga of ionic liquids.

$$M[Al_2(CH_3)_6X] + n\text{Aromatic} \underset{\text{low temp.}}{\overset{\text{high temp.}}{\rightleftarrows}} \underset{\text{liquid clathrate}}{M[Al_2(CH_3)_6X] \bullet n\text{Aromatic}} \qquad (3)$$

The genesis of ionic liquid development at the Air Force Academy was not red oil, chlorocuprates or liquid clathrates. It was missile batteries that started our interest in molten salts in general, then the lower melting ionic liquids in particular. The research at the Academy occurred during a period that went from almost no interest by the chemistry community to the present high level of activity in the field. While we make only a few claims about the importance of our findings in the area of ionic liquids, we definitely had a good seat from which to watch the field over the last 38 years. The rest of this history will be

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organized around the research done at the Air Force Academy in ionic liquids, and the work done by others that advanced the field.

A thermal battery is a primary battery with a high temperature molten salt electrolyte. It is activated by rapid heating with a pyrotechnic to a temperature sufficient to melt the electrolyte. This battery has an extremely long shelf life, especially for a primary cell. It also has a high current density, up to 1.5 A/cm^2 for short periods. The battery is used in applications where it must be stored in a device for a long period, then used to provide high power for a short time. The applications are primarily in weapons (missiles, artillery shells, nuclear warheads) and spacecraft. In fact, the battery was invented in Germany during World War II for the V2 rocket. The LiCl-KCl molten salt is used at the eutectic composition (58.5 mol % LiCl) at temperatures of 375°-550° C. This eutectic has a relatively low melting temperature compared to most simple inorganic salts, but is still high enough to cause problems with many materials it contacts. Also, the battery that contains the salt must be well insulated to protect temperature sensitive devices nearby.

In 1963 the Air Force Academy established a research laboratory that later was named the Frank J. Seiler Research Laboratory. The initial charter of the laboratory was to do basic research relevant to the technology needs of the Air Force in three general areas: chemistry, aeronautics, and applied math. Lowell A. King was among the first Chemistry Department faculty members assigned to propose and lead a research effort at the Seiler Laboratory. Since Lowell had done his PhD thesis on molten salt chemistry (under Fred Duke at Texas A&M), he proposed to address the high temperature problems in thermal batteries by devising a lower temperature eutectic salt electrolyte. This project clearly had industrial applications, since all thermal batteries were (and are now) manufactured by private industry.

The logic of the approach was that if the melting temperature of a salt like KCl could be reduced by hundreds of degrees by using a eutectic mixture, could it be lowered even further with some other eutectic? Perhaps as low as 100° C? The answer appeared to be the binary system NaCl-$AlCl_3$ and other alkali metal chloride mixtures with aluminum chloride. It was known at that time that the equimolar composition of NaCl-$AlCl_3$ had a melting point of 155° C, and that the nearby eutectic composition melted at 107° C(*7*). However, little was known about the chemical and physical properties of NaCl-$AlCl_3$, and the electrochemistry of potential battery electrodes was completely unknown. The group headed by King spent more than a decade carefully measuring properties of these not-quite-ionic-liquid molten salts, such as densities, conductivities, vapor pressures, and phase equilibria. The electrochemistry of solutes in the molten salt was also heavily studied.

Publication of reliable chemical and physical properties data was very important, since adoption of the electrolyte would not happen if users had to do

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this themselves. The Air Force Academy group started three very beneficial collaborations during those early years; with Robert Osteryoung, then at Colorado State University, with Gleb Mamantov at the University of Tennessee at Knoxville, and with Harald Øye at the Norwegian Institute of Technology in Trondheim. The institute headed by Øye had substantial expertise in properties of aluminum-containing molten salts, as a consequence of their close association with the aluminum industry in Scandinavia. They measured the viscosity of the NaCl-$AlCl_3$ system by an absolute method(*8*), and they showed from first principles that the junction potential of the Al/Al(III) reference electrode was negligible(*9*). That electrode was used by everyone studying chloroaluminate electrochemistry, and there was considerable debate about the electrochemical behavior of the electrode. Gleb Mamantov and G. Pedro Smith (at Oak Ridge National Laboratory) were pioneers in applying spectroelectrochemistry to molten salts, and made some fundamental discoveries about the speciation in the chloroaluminate melts(*10*). The collaboration with Osteryoung and his students in nearby Fort Collins, Colorado was especially fruitful, since they were one of the premier electrochemistry groups in the U. S.

The practical and industrial connection of the fundamental studies by those groups was always strong. During the 1970's Alcoa developed an aluminum smelting process utilizing the NaCl-$AlCl_3$ electrolyte, and tested it at pilot plant scale. Alcoa was not a formal partner with the Air Force Academy group, but there was considerable exchange of information. Gleb Mamantov's study of sulfur(IV) electrochemistry in NaCl-$AlCl_3$ spawned a small business, Molten Salt Technologies Inc., which still exists today. By the mid-1970's enough information was known about the chloroaluminate eutectics to prompt a battery manufacturer, the Eureka Co., to build and test some thermal batteries with the NaCl-$AlCl_3$ electrolyte. The batteries worked well and operated at a much lower temperature than the LiCl-KCl batteries, but unfortunately the company dropped their battery business to focus their attention on vacuum cleaners.

Mixtures of halide salts like NaCl with aluminum trichloride are termed chloroaluminates. They are not simple binary salts like LiCl-KCl. In fact in the molten state $AlCl_3$ is a molecular liquid, not an electrolyte. They are composed of the cation from the metal halide (Na^+ in this case) and a complicated mix of chloroaluminate anions $AlCl_4^-$, $Al_2Cl_7^-$, and Cl^- that are linked by equilibria whose constants are known(*11*).

The alkali metal chloroaluminate molten salts research was an excellent combination of basic research and practical applications, but the salts were not

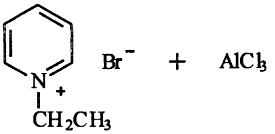

Figure 2. Hurley & Wier Ionic Liquid

ionic liquids by our current definition. Early in their work on molten salt electrolytes for thermal batteries, the Air Force Academy researchers surveyed the aluminum electroplating literature for electrolyte baths that might be suitable for a battery with an aluminum metal anode and chlorine cathode. They found references to work done at the Rice Institute by Frank Hurley and Thomas Wier on electrodeposition of aluminum in some $AlCl_3$–based molten salts that were liquid at room temperature(*12*). The electrolytes were mixtures of $AlCl_3$ and 1-ethylpyridinium halides, mainly the bromide (Figure 2). In 1968 the Air Force Academy group assembled cells with the aluminum and chlorine electrodes with various molten salt electrolytes, including a 1:2 ethylpyridinium bromide-$AlCl_3$ mixture that we would now term an ionic liquid(*13*). Except for ref. 13 and another electroplating paper published in 1952 (*14*) there was little interest in the pyridinium ionic liquids until much later.

In the mid 1970's both the Osteryoung group and the Air Force Academy group renewed their interest in the Hurley & Wier mixed haloaluminate ionic liquid. Chum, Koch, Miller and Osteryoung published a paper in 1975 on electrochemistry of some organometallic compounds that could not be done in the higher temperature NaCl-$AlCl_3$ molten salt, due to thermal sensitivity of the solutes(*15*). About the same time Nardi, Hussey, King and Erbacher used the same ionic liquid to selectively electrolyze the aluminum matrix away from Al_3Ni alloy fibers(*16*). Two of the people introduced in these papers would continue to be major figures in the ionic liquids field. Victor Koch founded Covalent Associates Inc., which is now commercially developing some ionic liquids. Chuck Hussey went from the Air Force Academy to the University of Mississippi, where he has made major finds in electrochemistry of metal ion complexes and alloy depositions in ionic liquids.

The next chapter in the ionic liquids story again involved both the Osteryoung and the Air Force Academy groups. The mixed bromide-chloride Hurley & Wier salts were replaced in 1978 by the 1-(1-butyl)pyridinium chloride - $AlCl_3$ ionic liquid (Figure 3), which was easy to prepare and had superior physical properties. The Colorado State University group was first to publish a paper using this new electrolyte(*17*), but the Air Force group got the patent(*18*). The BPC-$AlCl_3$ salt looked like it could be an excellent battery electrolyte, as well as a useful medium for spectroscopy and synthesis. But, as in the case of

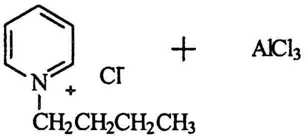

Figure 3. BPC-$AlCl_3$ Ionic Liquid

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the NaCl-$AlCl_3$ molten salt, the physical, chemical, and electrochemical properties of this new material had to be measured and published before anyone else would be much interested in using it. The physical properties, such as density, viscosity, and conductivity were done at the Air Force Academy(*19*), the early spectroscopy at Colorado State University (*17*), and many electrochemical experiments were done at both places.

The Raman spectroscopy study in ref. 17 showed that the equilibria between chloride and various chloroaluminate anions (and Al_2Cl_6) found in NaCl-$AlCl_3$ molten salts also pertained in the lower melting BPC-$AlCl_3$ system. That paper, by the way, was the first written by Bernard Gilbert on ionic liquids. His later very careful spectroscopic studies of other ionic liquids have been important in the understanding and advancement in this field. One important difference between the NaCl-$AlCl_3$ and the BPC-$AlCl_3$ liquids (besides melting temperatures) were the magnitudes of the equilibrium constant for the chloroaluminate anion reactions. A potentiometric determination of the equilibrium constant for the reaction that relates $AlCl_4^-$, $Al_2Cl_7^-$, and Cl^- gave a value of 3.8 X 10^{-13} (*20*). This implies that the chloride activity changes about thirteen orders of magnitude near the 1:1 BPC:$AlCl_3$ equivalence point.

The author of this chapter joined the Seiler Research Laboratory at the Air Force Academy at about the beginning of the BPC-$AlCl_3$ era in 1973, and replaced Lowell King as the PI of the molten salts group upon his retirement.

The BPC-$AlCl_3$ ionic liquid has two unfortunate features. First, the melting temperature of the equimolar composition is 40° C, so it is not an ionic liquid at the composition that has the highest conductivity. Second, in the basic compositions ($AlCl_3$ mole fraction <0.5) the butylpyridinium cation is easily reduced. This fact results in a much more narrow electrochemical window than NaCl-$AlCl_3$, and an incompatibility with Al electrodes. This prompted us to search for a salt with even lower melting temperatures, which would contain a cation that was substantially more difficult to reduce. The approach to lower melting points was based on a rather intuitive explanation for the abnormally low melting temperatures of chloroaluminate salts in general. As explained earlier, the formation of a chloroaluminate binary salt involves the formation of $AlCl_4^-$, $Al_2Cl_7^-$ and in very $AlCl_3$-rich melts $Al_3Cl_{10}^-$ anions. The mixtures of large anions with many degrees of freedom should inhibit crystallization until much lower temperatures. The ionic liquids with large cations in addition to large anions should have even lower melting points, which is exactly what is observed. Asymmetry in the cation should also result in lower melting temperatures by this argument.

Predicting the reduction potentials of the cations had a more quantitative basis. At just about the time we were searching for less easily reduced cations, M. J. S. Dewar at the University of Texas released the software for performing MNDO semi-empirical molecular orbital calculations (MNDO =

Modified Neglect of Differential Overlap). The method was extremely fast, since the core electron energies were parameterized with thermodynamic data, and did not have to be calculated as in *ab initio* methods. The practical result was that molecules or ions the size of pyridinium cations could be calculated in just a week or two on the main frame computers of the late 1970's(*21*). The output of the calculations contained an optimized geometry, the heat of formation, and the energies of all orbitals. We reasoned that the energy (reported in eV) of the highest occupied molecular orbital (HOMO) would be roughly correlated with the electrochemical oxidation potential in solution, and the lowest unoccupied molecular orbital (LUMO) energy would correlate with the electrochemical reduction potential (E_{red})(*22*). In 1979 Chuck Hussey (then moved to the University of Mississippi) and I embarked on several months of calculations, syntheses, and half-wave potential measurements of many new cation candidates for room temperature molten salts (Figure 4). The types of cations considered then were (R = alkyl groups or H):

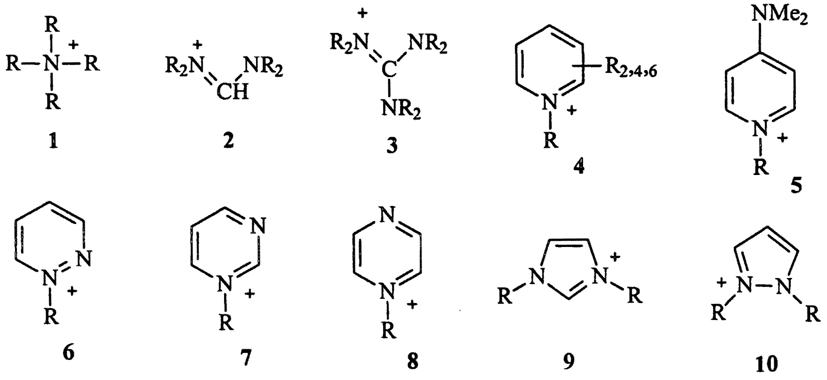

Figure 4. Cation Candidates

We plotted the calculated LUMO energies of these types of cations against the half-wave reduction potentials ($E_{1/2}$) that we found in the literature or we measured. The plot has considerable scatter, because the published $E_{1/2}$ values varied by several hundred millivolts for the same compound. Nevertheless, we obtained a straight-line fit that has a unit slope. Compounds of type **1** have the largest negative $E_{1/2}$, and the 1,3-dialkylimidazolium cations (**9**) were predicted to reduce 0.9 V more negative than the 1-alkylpyridinium cations (**4**). We submitted these predictions for publication, but the work was rejected as being "too obvious." It wasn't so obvious to me, since I was surprised by the answer. We took the easy route of publishing it as a government technical report(*23*).

A quick search of Beilstein showed us that halide salts of numerous examples of the dialkylimidazolium cation were prepared in the 1880's in

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Germany(*24*). The iodides were simple to prepare in one step from commercially available starting materials, then the chloride salts were obtained by ion exchange. We soon found that the chlorides could be made directly in one step(*25*). When a dialkylimidazolium chloride salt (1-ethyl-3-methylimidazolium chloride, EMIC, for example) was mixed with aluminum chloride, an ionic liquid was formed that had a freezing point below room temperature for all compositions between 0.33 and 0.67 $AlCl_3$ mole fraction. Furthermore, the imidazolium cation in these melts was more stable toward electrochemical reduction by –0.9 V compared to the alkylpyridinium cations. This was exactly as predicted by the MNDO calculations(*26*). Soon after this we measured the phase transitions, densities, viscosities and conductivities of chloroaluminate ionic liquids made from a series of dialkylimidazolium chlorides with varying lengths of alkyl substituents(*27*). We finally settled on the ionic liquids containing the 1-ethyl-3-methylimidazolium cation as the best compromise of ease of synthesis and physical, chemical and electrochemical properties (Figure 5).

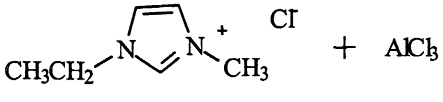

Figure 5. EMIC-AlCl$_3$ Ionic Liquid

We still considered battery electrolytes as the practical industrial application of these ionic liquids. In fact we explored a number of battery concepts employing these electrolytes(*28*), as did several other groups in the U. S. and Japan(*29*). To my knowledge no battery company has actually brought to market a battery with this or any other ionic liquid electrolyte. James Auborn of Bell Laboratories (now Lucent Technologies) spent two weeks working at the Air Force Academy as a naval reservist, and he took the EMIC-$AlCl_3$ salt back with him to study aluminum deposition(*30*). At about the same time Nisshin Steel Co. had been developing a continuous process for electroplating steel in the EMIC-$AlCl_3$ electrolyte on a pilot plant scale, which clearly involved the first large scale production of this ionic liquid(*31*).

Not too long after publication of our initial work on the EMIC-$AlCl_3$ ionic liquid, the Air Force's scientific liaison office in London arranged a visit to the Air Force Academy by a young academic named Ken Seddon. He was attracted to this new medium by its very high but adjustable chloride content in total absence of water, as well as its suitability as a spectroscopic solvent. By coincidence Chuck Hussey was visiting the Air Force Academy at the same time, an event that resulted in a long-term collaboration between the Mississippi and Sussex (now Belfast) groups. The room temperature chloroaluminate medium

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did in fact allow for the preparation of metal ion chloro-complexes that had not been seen before(*32*). The story of how this esoteric interest in inorganic complexes became QUILL, a major facilitator for industrialization of ionic liquids in general, is a story best told by Ken Seddon if he writes a chapter such as this one.

Earlier in this account I pointed out Harald Øye's productive collaboration with the Air Force Academy group on the physical properties measurements of the high temperature chloroaluminate molten salts, such as NaCl-$AlCl_3$. In 1986-87 he came to Colorado Springs for a yearlong sabbatical from Trondheim to study our lower melting salts. He pointed out that the vapor pressure of the EMIC-$AlCl_3$ is curiously much lower than NaCl-$AlCl_3$. This was shown qualitatively by the observation that if you heat a tube of $AlCl_3$-rich NaCl-$AlCl_3$ (say $X_{AlCl_3} = 0.67$) to about 200° C, then $AlCl_3$ will distill from the salt and condense in a cooler part of the tube. This does not occur with EMIC-$AlCl_3$ with the same $AlCl_3$ content and at the same temperature. Øye carefully measured the low vapor pressures (caused by volatile Al_2Cl_6) of the EMIC-$AlCl_3$ melts, and combined the results with some potentiometric data we had collected earlier. The result was a quantitative thermodynamic model of the EMIC-$AlCl_3$ system that showed that it was much more ionic than the chemically similar alkali halide-aluminum chloride systems. That is, the liquids with organic cations have less Al_2Cl_6, and more $Al_3Cl_{10}^-$ and $Al_4Cl_{13}^-$(*33*).

Ionic liquids containing $AlCl_3$ seemed to be a natural medium for organic reactions that are catalyzed by Lewis acids, such as Friedel-Crafts reactions. We knew that aromatic compounds were quite soluble in the EMIC-$AlCl_3$ ionic liquid, and we soon found that alkylation and acylation reactions worked well in the ionic liquid solvent(*34*). Actually, the medium was both solvent and catalyst, where the Lewis acidic species $Al_2Cl_7^-$ was a component of the salt and the catalyst. The advantages were that the catalytic activity was easily controlled, the reaction was homogeneous, product isolation was easy, and there was none of the chlorinated hydrocarbon solvent commonly used in Friedel-Crafts reactions. Many other researchers have found more catalytic reactions in ionic liquids, and some of these very likely will be the most important industrial use of ionic liquids in the future.

In 1990 Mike Zaworotko took a sabbatical leave from St. Mary's University in Halifax. That year spent at the Air Force Academy introduced a new dimension to the growing field of ionic liquid solvents and electrolytes. The electrolytes we had worked with to date had all been based on $AlCl_3$ (or $AlBr_3$), which meant that they reacted with water. Zaworotko proposed to prepare and characterize low melting salts that still had the dialkylimidazolium cation, but had water-stable anions. The new tetrafluoroborate, hexafluorophosphate, nitrate, sulfate, and acetate salts (Figure 6) turned out to be very easy to make, and they were stable (at least at room temperature) towards hydrolysis(*35*). I

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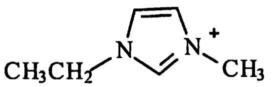

BF_4^-, PF_6^-, NO_3^-, CH_3COO^-, SO_4^{2-}

Figure 6. Early water stable ionic liquids

wonder why nobody thought of these earlier. We thought of these salts as candidates for battery electrolytes, but they (and other similar salts) have proven more useful for other applications(*36*).

In 1992 Richard Carlin took over leadership of the ionic liquids group (we still called them room temperature molten salts) at the Seiler Research Laboratory of the Air Force Academy. (I remained nearby, but in a management position). Others in the group at that time were Joan Fuller, Hugh DeLong and Paul Trulove; all of whom have continued to work in the ionic liquids field. Carlin and I had collaborated on the issue of reversible lithium deposition in the chloroaluminate ionic liquids while he was at the University of Alabama. This is obviously a topic of great interest for battery applications, because of the high energy density of the lithium electrode. On the face of it, one would not expect Li(I) to be reducible to Li metal in an electrolyte that contains Al(III), especially where the Al(III) is in very high concentration as the solvent and supporting electrolyte. Nevertheless, we found that when the ionic liquid is buffered at the Lewis neutrality point(*37*), then Li (and even Na) could be electrodeposited(*38*).

Lithium batteries with metallic lithium electrodes can store huge amounts of energy, but large sized batteries have fallen into disfavor due to the hazards involved with elemental Li and the difficulty in making a rechargeable cell. Lithium-ion rechargeable batteries are now the commercial favorites, although the military still uses metallic Li cells extensively. In Li-ion cells, the lithium is intercalated in a carbon matrix during the charging process, then released by the de-intercalation followed by transport through a Li^+-conducting electrolyte to be intercalated in a chalcogenide matrix. Carlin and coworkers devised a similar battery cell where the component cations and anions of an ionic liquid are intercalated and deintercalated in carbon during charging and discharging. This dual intercalating molten electrolyte (DIME) battery concept uses the ionic liquid both as electrolyte and energy-storing electrode material(*39*). The principal of this simple battery cell can be best understood with an example using one of the earliest of the low temperature ionic liquids; $EMI^+AlCl_4^-$. The overall electrochemistry is

$$EMI^+ + AlCl_4^- + (x+y)C \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} \underset{\text{“negative”}}{[EMI]C_x} + \underset{\text{“positive”}}{[AlCl_4]C_y} \qquad (4)$$

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The positive and negative terminology uses the rechargeable battery convention and the [] brackets denote intercalation.

In 1948 the first chloroaluminate ionic liquids were made and used for electrodeposition of aluminum. Electrodeposition is once again becoming an important use of ionic liquids. Chuck Hussey at the University of Mississippi and Gery Stafford at the National Institute of Standards and Technology have found that some interesting alloys may be plated from ionic liquid electrolytes(*40*).

The foundation for the industrial future of ionic liquids is being laid by the people working on the large-scale industrial chemical processes that might be done in ionic liquids. An early example of this was the catalytic alkene dimerization process worked out by Chauvin and Olivier-Bourbigou(*41*). The literature of industrial reactions amenable to ionic liquid solvents is expanding rapidly. The chemical engineering of ionic liquids is another important dimension of their use in industry. The industrial implementation of ionic liquids will not be discussed in this paper, since that is the topic for this entire volume. It is abundantly clear that the rise in interest in industrial applications of ionic liquids has paralleled the increased attention to the environmental impact of the chemical process industry. The response to this, currently called Green Chemistry, will continue to motivate research in ionic liquids and other substitutes for media currently in use in the chemical process industry. The way to get from the past, through the present and on to the future will undoubtedly happen like all major technologies have developed in the last century. That is, a combined investment and effort by industry, government and academia. Coordinating groups like the QUILL in Belfast and the Center for Green Manufacturing in Tuscaloosa will be important in bringing together the elements (literally and figuratively) for applying ionic liquids to industrial problems.

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22. Strictly speaking there should be no LUMO energy, since by definition the orbital has no electrons. The values reported by MNDO and most other computational methods are artifacts of the calculations. However, they are useful artifacts that often are practical to use. See Cook, David B.

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Chapter 18

Significance of Cations in Ionic Liquids Chemistry

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There is a tendancy to classify ionic liquids either as individual solvents (LiCl–KCl vs. NaCl–KCl, $NaNO_3$–KNO_3 vs. $LiNO_3$–KNO_3) or in terms of the anions. In fact, a compromise is appropriate. We shall point out how the cation choice influences the chemistry, including the electrochemistry, of an anion in an ionic liquid. Some examples follow. The effect of the cation on the structure of liquid alkali halides is exemplified by the coordination chemistry of dissolved Ni(II) as well as by diffraction studies. Raman spectroscopy demonstrates the cation influence on the fundamental equilibrium $2AlCl_4^- \rightarrow Cl^- + Al_2Cl_7^-$ in alkali chloroaluminates. When the electrochemical reduction of NO_3^- in alkali nitrates is examined, we observe product dependence that can be traced back to metal + oxygen reactions. Regarding the Lewis acidity of room temperature ionic liquids, it has been shown that the cracking of alkanes and the dissolution of heavy oil are influenced by the cation present with a given haloaluminate.

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

This is a cautionary tale. We will attempt to point out the relationship of the old "molten salts" research to the new "ionic liquids" research and to demonstrate the strengths and weaknesses of classifying ionic liquids by the nature of the anions - a situation quite pronounced for the older literature but not to be ignored for ambient temperature systems.

What is an Ionic Liquid?

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The glib definition is a liquid composed totally of ions with the forces overwhelmingly coulombic – a relaxed simple ionic crystal such as KCl. Indeed, most ionic liquids are salts but there are intriguing situations such as the salt $HgCl_2$ which has very low conductivity in the liquid state and the molecule PCl_5 which turns out to be ionic (PCl_4^+ PCl_6^-) in the solid. There are also ionic liquids such as emimAlCl$_4$ and its mixtures with emimCl where there is evidence of considerable hydrogen bonding between the emim$^+$ and the anions (emim=1-ethyl-3-methyl-1*H*-imidazolium). Then we have systems in which ionization is incomplete or significant ion pairing occurs. One might arbitrarily define an ionic liquid as one in which more than half the "molecules" are ionized or one could be even less precise and talk about a liquid in which the chemistry is primarily determined by the ions even though they are in a minority e.g. the 28 mol% KOH of the Stuart electrolyzer (*1*). We are then concerned with the chemistry of electrolyte solutions where the solvent itself is molecular but ionizing.

Simple Ionic Salts as Solvents

In this section we will discuss a variety of examples of medium to high temperature ionic liquids in which the cations are obviously far more than spectator ions viz. basic physicochemical properties and structure, electronic spectra of dissolved transition metal ions and some thermodynamic properties and electrode reactions of nitrates.

Basic Physicochemical Properties and Structure

Over 40 years ago, X-ray diffraction studies showed that the melting of simple alkali halides produced liquids with alternating anions and cations and average first coordination numbers showing the effects of radius ratios (*2*). Neutron diffraction is commoner for this work now and details beyond the first "sphere" can be well matched by theoretical calculations (*3*). We must be careful in assigning any meaning or precise structure to a given set of numbers. We also can learn of structural changes in a series of liquids from measurements of viscosity and conductivity. These two quantities are expected to move in opposite directions with a change of one ion component although the charge aspect of conductivity need not always correlate with size.

Electronic Spectra of Dissolved Transition Metal Ions

An examination of the UV-visible spectra of the 3d ions in the single solvent LiCl-KCl (*4*) indicated that Cr(III) is octahedrally coordinated, Fe(II), Co(II) and Mn(II) tetrahedrally coordinated, Cu(II), Cr(II) and Ni(II) take up distorted tetrahedral geometry and Ti(III), V(III) and V(II) exist in equilibrium mixtures of octahedral and tetrahedral sites (but apparently not in 5-coordination). The situation with Ni(II) was studied in considerable detail ($NiCl_2$ in LiCl-KCl at different temperatures (*5*), $NiCl_2$ in 5 individual alkali chlorides (*6*), $NiCl_2$ in various CsCl-$NiCl_2$ (*7*), CsCl-$ZnCl_2$ (*8*) and LiCl-KCl (*9*) mixtures) with the conclusions that in most liquid chlorides the Ni^{2+} ion is found in both wel-defined tetrahedral (T) and less-defined octahedral (O) sites; it was suggested that larger cations form the shell around the T sites and the smaller cations e.g. Li^+, polarize the chlorides of the O sites, with increasing temperature favoring T site formation and occupation. Figure 1 shows a selection of these spectra compared with that for tetrachedral $NiCl_4^{2-}$ in an organic salt (*10*). For detailed discussions see (*11*).

Thermodynamic Properties and Electrode Reactions of Nitrates

Measurements of the e.m.f.s of cells of the type

$$Ag/AgNO_3/AgNO_3(N) \text{ in } MNO_3/Ag$$

where the mole fraction N is given by $10^{-4}<N<10^{-2}$ indicated negative deviations from Raoult's law for M=K, positive deviations for M=Li, Na, Li+Na and Li+K, and virtual ideality for the $NaNO_3$-KNO_3 eutectic solvent (*12*). The work constants, W, at 350° C ranged from -2.7 to +4.0 kJ mol^{-1*} suggesting a relative insensitivity of the silver ion to its next nearest neighbors.

However, if we examine the electrochemical reduction of alkali nitrates, the cation identity is much more important. Table I lists some of the electrode and following reactions observed in these systems as well as some thermal processes.

*The work constant derives from the theory of regular solutions viz. $RT\ln\gamma_N = W(1-N)^2$ where γ_N is the activity coefficient at mole fraction N.

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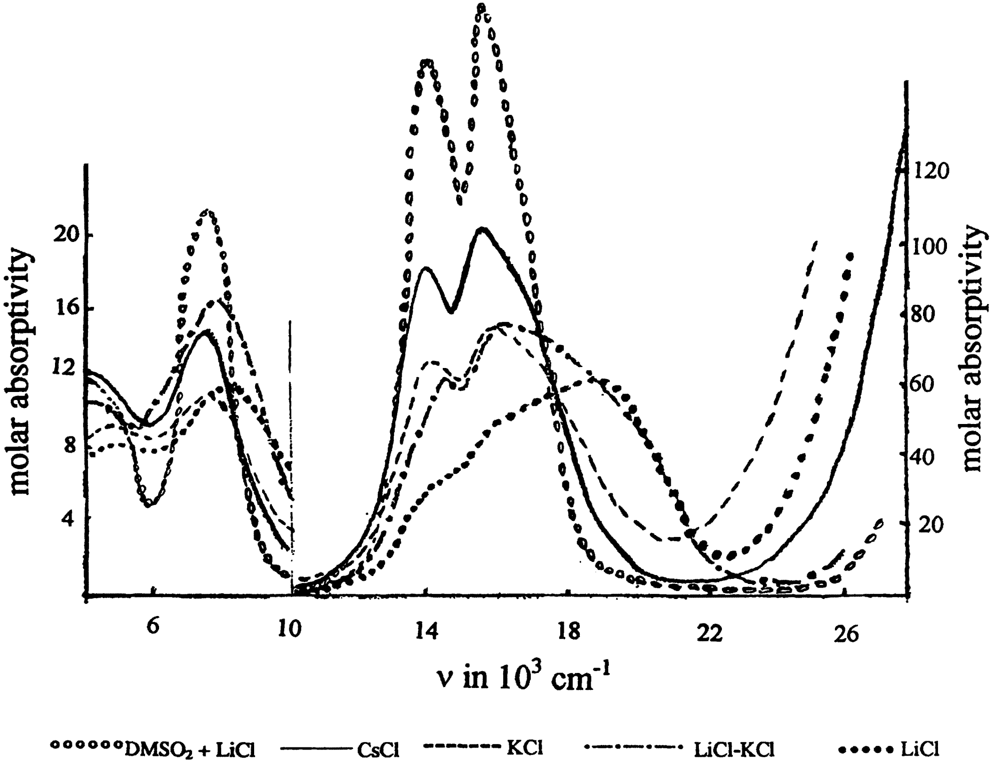

Figure 1. *UV-Visible Spectra of* $NiCl_2$ *solutions in various solvents. Adapted from references 6, 9 and 10.*

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

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Table I. Some Liquid Nitrate Reactions

Equation No.	*Nitrate Reactions*
1.	$NO_3^- \longrightarrow NO_2^- + \frac{1}{2}O_2$
2.	$M^+ + e^- \longrightarrow M$
3.	$NO_3^- + 2e^- \longrightarrow NO_2^- + O^{2-}$
4.	$NO_3^- + O^{2-} \longrightarrow NO_2^- + O_2^{2-}$
5.	$2NO_3^- + O_2^{2-} \longrightarrow 2NO_2^- + 2O_2^-$
6.	$O^{2-} + H_2O \longrightarrow 2OH^-$
7.	$H_2O + NO_3^- + 2e^- \longrightarrow NO_2^- + 2OH^-$
8.	$2M^+ + O^{2-} \longrightarrow M_2O\downarrow$
9.	$NO_3^- + e^- \longrightarrow NO_2 + O^{2-}$
10.	$NO_3^- + 5e^- \longrightarrow \frac{1}{2}N_2 + 3O^{2-}$
11.	$Pt(electrode) + M + NO_3^- \longrightarrow Pt(NO)^{3+} + 2O^{2-}$
12.	$NO_3^- - e^- \longrightarrow NO_2 + \frac{1}{2}O_2$

Voltammetric studies of alkali nitrates coupled with chemical analysis of the products of coulometry show the reduction of nitrate to nitrite at ~-1.5 V vs. Ag^+/Ag (*13, 14, 15*). When Li^+ or Na^+ are the counterious (as pure salts or eutectic components) this process is inhibited by oxide film formation (activation energy ~60 kJ mol^{-1}) and one observes a sharp current increase at ~-3 V with dissolution of a platinum electrode (*14, 16*).

It was shown that in dry liquids this first electrode reduction to oxide and nitrite (Eqn. 3) is followed by chemical oxidations of oxide to peroxide (for M=Li, Na, or K) (Eqn. 4) and to superoxide (Eqn. 5) (for M=Na and especially K) (*17, 18, 19*). In addition, the oxides Li_2O and Na_2O are sparingly soluble in the liquid nitrates, thus inhibiting the electrode reactions by film formation (Eqn. 8). Only traces of NO_2 are seen at the cathode. If water is present (its solubility is ~10^{-3} M) then a catalytic nitrate reduction is seen before the direct process and some peroxide (and superoxide) is destroyed. Alkali metal ion reduction does indeed occur at very negative potentials but leads to the corrosion of most electrode materials (Equation 11 is a feasible process). If we recall the oxygen chemistry of the alkali metals the differences between the nitrates make sense: Li_2O, Na_2O_2 and KO_2 are the favored products of the M/O_2 reactions.

[1] The electrochemical reduction of ClO_4^- in liquid $LiClO_4$ (*20*) similarly leads to the fomation of insoluble Li_2O but it is possible to build up a film of Li behind the Li_2O at more negative potentials and this Li can react EXPLOSIVELY with the bulk perchlorate!

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Haloaluminate and Hydrogen Halide Systems

Haloaluminate systems (ZX/AlX_3) are controlled by equilibria of the type illustrated in Table II for X≡Cl. Theoretical calculations (*21*), which apply to the GAS PHASE at 298 K, gave a value for the equilibrium constant $\underline{K}$ for reaction 5, the fundamental one, of 7×10^{32}. Experimental estimates of this quantity with the necessary inclusion of the counter ions, Z^+, are $\sim 10^7$ for liquid Na^+ salts at 598 K (*22*) and $\sim 10^{16}$–10^{18} for liquid emim$^+$ salts at 298 K (*23*). The magnitude of $\underline{K}$, even at 598 K, allows for the clear division of systems of this type into Lewis basic ($X_{ZCl} > X_{AlCl_3}$) and Lewis acidic ($X_{AlCl_3} > X_{ZCl}$) systems with their divers chemistries. Hydrogen halides in these systems in turn behave as Brönsted acids (in Lewis basic liquids) or superacids (in Lewis acid liquids). For the pure hydrogen halides there is evidence, both theoretical and experimental (*24*), for the formation of species $H_nX_{n+1}^-$ (n = 1-4) and $H_{m+1}X_m^+$ (m = 1,2) while within the haloaluminate liquids polyhalahydrogenate (1-)anions and haloaluminate - hydrogen halides have been observed or proposed (*25, 26*). These adducts are further examples of the established line of hydrogen-bonded anions QHR^- with Q = halide and R = haloaluminate. Table II includes examples of these equilibria for chlorides.

The nature of the cation Z^+, besides determining $\underline{K}$, influences the struture and reactivity of the chloroaluminate liquids in several ways. The melting points follow from the lattice energies which are much lower for organic than for simple inorganic salts. Within the alkali metal series (*27*), it was shown by Raman spectroscopy that (*i*) within the $AlCl_3$-LiCl system, $AlCl_4^-$ and Al_2Cl_6 persist to $X_{AlCl_3} = 0.75$; (*ii*) higher chloroaluminate polymer formation increases in the order $Li^+ < K < Cs^+$; (*iii*) $CsAl_2Cl_7$ shows pronounced dissociation into $CsAlCl_4$ and $CsAl_3Cl_{10}$; (*iv*) Li^+ interacts sufficiently with $AlCl_4^-$ to distort its normal tetrahedral geometry. Thus the contrast between the small polarizing Li^+ and the large non-polarizing Cs^+ is apparent in the anionic speciation and structure.

Organic cations are more than overgrown cesium ions. Those used in combination with haloaluminates include the 1-alkyl-3-methyl-1*H*-imidozolium ions ($1m^+$), the unsubstituted and N-substituted pyridinium ions and the trialkyl sulfonium ions (not necessarily with all alkyl groups the same). The imidazolium cations are able to hydrogen bond to halide ions, particularly at the 2-position but also at the 4- and 5- positions: this give rise to the higher viscosity and lower conductivity of basic haloaluminate liquids (changes which are linear in mole fraction up to $X_{AlCl_3} = 0.5$) and the smooth variation of ring proton chemical shifts with X_{AlCl_3}. Further, the values of viscosity, ring proton chemical shifts and infrared vibration frequencies indicate a corresponding behavior of emim$^+$ in the liquids emimCl:HCl ($0.38 < X_{HCl} < 0.68$) (*28, 29, 30*). The earlier-developed but less-studied N-alkylpyridinium ions show similar hydrogen-bonding capabilities and the stacking of layers of alternating cations and basic anions has been proposed.

Table II. Chloroaluminate and Hydrogen Chloride Based Equilibria

Equation No.	*Cloride Reactions*
1.	$2AlCl_3 \longrightarrow Al_2Cl_6$
2.	$Cl^- + AlCl_3 \longrightarrow AlCl_4^-$
3.	$AlCl_4^- + AlCl_3 \longrightarrow Al_2Cl_7^-$
4.	$Al_2Cl_7^- + AlCl_3 \longrightarrow Al_3Cl_{10}^-$
5.	$\mathbf{Cl^- + Al_2Cl_7^- \longrightarrow 2AlCl_4^-}$
6.	$Cl^- + HCl \longrightarrow HCl_2^-$
7.	$HCl_2^- + HCl \longrightarrow H_2Cl_3^-$
8.	$H^+ + HCl \longrightarrow H_2Cl^+$
9.	$H_2Cl^+ + HCl \longrightarrow H_3Cl_2^+$
10.	$3HCl \longrightarrow HCl_2^- + H_2Cl^+$
11.	$\mathbf{Cl^- + H_2Cl_3^- \longrightarrow 2HCl_2^-}$
12.	$AlCl_4^- + HCl \longrightarrow \underline{ClHCl}AlCl_3^-$
13.	$Al_2Cl_7^- + HCl \longrightarrow \underline{ClHCl}Al_2Cl_6^-$
14.	$\underline{ClHCl}AlCl_3^- + Al_2Cl_7^- \longrightarrow AlCl_4^- + \underline{ClHCl}Al_2Cl_6^-$

Trialkylsulfonium salts have not been investigated over wide $AlCl_3$ mole fraction ranges - certain systems form liquids at ambient temperatures with excess aluminum halides or with hydrogen halides ($X_{HX} > 0.5$) (*31, 32*). These cations offer neither hydrogen bonding nor aromatic character and thus provide a useful comparison for some reactions.

Simple pyridinium salts present other possibilites through their onium character. It has been shown that pyridinium chloride itself (M. Pt. 144°) can play the role of a Brönsted acid in cleaving alkyl aryl ethers (*33*), can form anions $H_nCl_{n+1}^-$ with HCl and can form cations $pyHClHpy^+$ in which the protons on nitrogen are NOT exchangeable (on the ^1H NMR time scale) with those of

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$H_nCl_{n+1}^-$ (*34*). The species $pyHClHpy^+$ may be thought of as H_2Cl^+ (Equation 10 of Table II) stabilized by pyridine. We have shown that acidic pyridinium chloroaluminate liquids (X_{AlCl_3}. > X_{pyHCl}).crack long-chain alkanes, giving rise to branched C_4–C_7 alkanes (see Figure 2) and lesser amounts of alkenes (*35*). These liquids are also capable of dissolving heavy oils (*36*) with a significant reduction in the higher molecular weight (hence higher boiling) components (Figure 3). This superacidic behavior is also shown by the acidic haloaluminates of the other cations ($emim^+$, $bmin^+$, R_3S^+, $N\text{-}Bupy^+$) but their rates of reaction are less. Furthermore, although the presence of protons as $ClHClAl_2Cl_6^-$ enhances the reactivity, it is not essential: cracking still occurs when this proton type is reduced to below electrochemical detection limits by MAC (methylaluminum sesquichloride) which does not attack pyH^+! While basic haloaluminate mixtures do not crack alkanes, salts of HX_2^- (with Hammett acidities comparable to that of concentrated hydrochloric acid) show some reactivity but at too low a level at 25°C to distinguish cationic differences.

In making comparisons of the reactivity of various haloaluminate systems, it has been customary to think in terms of first the mole fraction of $AlCl_3$ and then those of the anions present e.g. $AlCl_4^-$ and $Al_2Cl_7^-$ in Lewis acidic mixtures. We have calculated the molarities of the ions for a number of mixtures (Table III) in order to ascertain whether concentration is a more appropriate quantity to consider in making such evaluations: clearly the concentrations of given anions are influenced by the sizes of the counter-cations.

Table III: Mole percentage and molarity of anions in different chloroaluminate ionic liquid systems:

	$AlCl_3$ Mole %	*Density (g mL^{-1})*	*$\overline{MW}$*	*$M_{AlCl_4^-}$ (mol/L)*	*$M_{Al_2Cl_7^-}$*	*Ref*
emim Cl	50.00	1.2941	279.94	4.62	0	29
MW:146.6	54.99	1.3209	309.51	3.32	0.95	
	60.01	1.3488	346.69	1.94	1.95	
	66.66	1.3888	413.20	0	3.36	
Me_3SCl MW:112.5	66.66	1.40	378.78	0	3.69	38
Me_3SBr^* MW:157	66.66	1.59	423.28	0	3.75	32
Et_3SBr^*	50.00	1.4116	332.34	4.25	0	37
MW:199	54.99	1.4286	361.97	3.07	0.88	
	60.01	1.4455	399.01	1.81	1.81	
	66.66	1.4680	465.28	0	3.15	

* For the mixed halogen systems we have ignored exchange and we quote molarities of $AlCl_3Br^-$ and $Al_2Cl_6Br^-$. Note: NaCl with a formula weight of 58.5 has a molarity of 26.6 at the temperature of 801°C.

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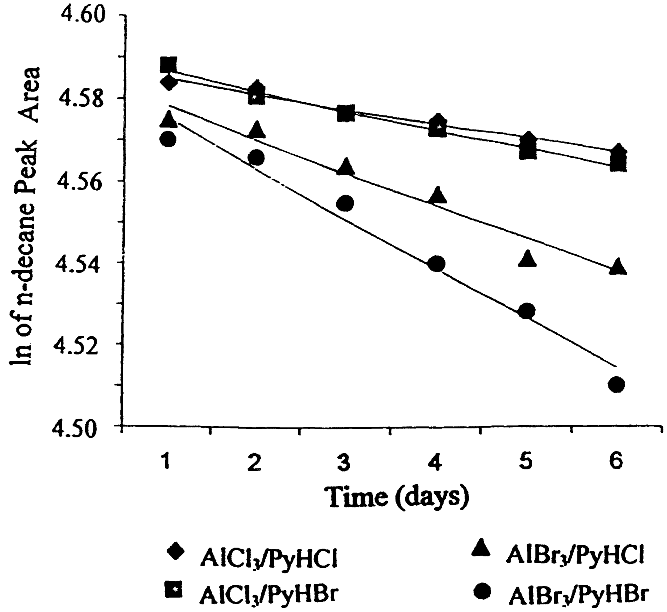

Figure 2. The cracking of n-*decane by different haloaluminate liquids, each containing 66% aluminum halide.*

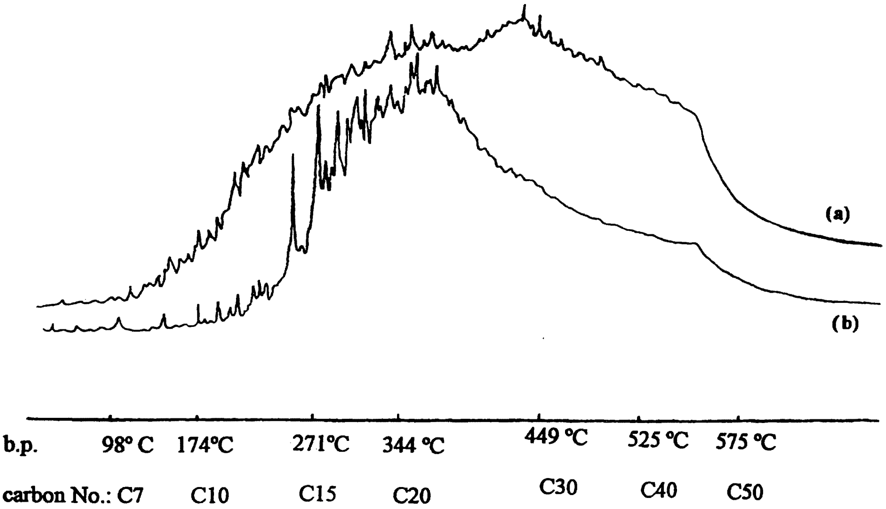

Figure 3. Boiling point distribution curve of Plover Lake heavy oil sample before (A) and after (B) treatment with an acidic pyridinium chloroaluminate liquid.

Conclusion

We see that in ionic liquids, the chemistry of compounds with a given inorganic anion is determined by several factors. The structure and freezing point follow from the lattice energy and radius ratio in the simplest cases but organic cations offer the possibility of hydrogen bonding to selected anions (Cl^- not $Al_2Cl_7^-$) and complex structures. Further, small cations can polarize large anions giving rise to anion distortions as illustrated by the electronic spectra of dissolved Ni(II) species and the Raman spectra of haloaluminates. Pure anion equilibria and electrode reactions do not stand alone and their energetics can be highly sensitive to the nature of the counter ion(s).

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Chapter 19

Dynamic Supramolecular Chemistry: The Role of Hydrogen Bonding in Controlling the Selectivity of Diels–Alder Reactions in Room-Temperature Ionic Liquids

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The Diels-Alder cycloaddition reaction between methyl acrylate and cyclopentadiene has been investigated in a number of air and moisture stable ionic liquids. The *endo/exo* ratio of the reaction has been used as a probe of the nature of the solvents. We have demonstrated that hydrogen bonding between the cation of the ionic liquid and the methyl acrylate is the principal interacting controlling the product selectivity.

Introduction

Room-temperature ionic liquids are liquids that are constituted entirely of ions. Hence, they provide a solvent environment that is quite unlike any other available at room temperature. They have recently excited much interest in synthetic and catalytic chemistry.[1] However little is known about how the use of an ionic liquid solvent can effect the reactions of solute species. With their unique character, the ionic liquids may induce solvent effects on a wide range of processes. Hence, the investigation of the effect of the solute microenvironment of reactivity in these solvents forms a central theme in our research. In this paper we report, for the first time, how a specific solvent-solute interaction in room-temperature ionic liquids can lead to changes in both the rate and product selectivity of a reaction.

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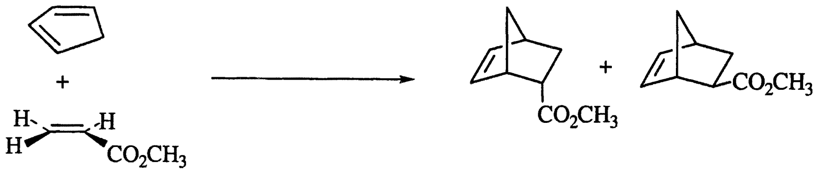
The Diels-Alder reaction remains one of the most useful carbon-carbon bond-forming reactions in organic chemistry. It is highly “atom efficient but suffers from being an addition process with a negative entropy of reaction. As such, the use of high temperatures to give useful reaction rates has a detrimental effect on the position of the reaction equilibrium. Hence, there is a great deal of interesst in accelerating Diels-Alder reactions at low temperatures. Solvents offer one of the ways in which these reactions may be manipulated. Here we are using the reaction of cyclopentadiene with methyl acrylate, which leads to a mixture of *exo* and *endo* products as a probe of the solvent behaviour. We have previously reported some initial results of this investigation[2] and others have reported similar reactions in ionic liquids.[3,4,5,6]

The reaction of cyclopentadiene with methyl acrylate has been widely investigated in a range of molecular solvents and solvent influences on the *endo/exo* selectivity of the reaction are well known. They may be viewed as being due to the “polarity” of the solvent leading to the stabilisation of the more polar (*endo*) activated complex.[7] The effect has also been attributed to solvophobic interactions that generate an “internal pressure” and promote the association of the reagents in a “solvent cavity” during the activation process.[8] As highly ordered hydrogen-bonded solvents, ionic liquids have the potential to be high internal pressure solvents and to have dramatic effects on Diels-Alder reactions. Although not only a solvent effect, the addition of a Lewis acid is also known to have a dramatic effect on these reactions.[9]

Results

In this paper we seek to determine how ionic liquids affect the progress of the addition of methyl acrylate to cyclopentadiene (Scheme 1). In a typical reaction, methyl acrylate and cyclopentadiene, both freshly distilled, were added to the freshly dried ionic liquid directly and the mixture was stirred at 25 °C for 72 hours. The product was extracted from the ionic liquid with either diethyl ether leaving the pure ionic liquid, which can be reused.



Scheme 1. The reaction of cyclopentadiene and methyl acrylate

Table I shows the *endo/exo* selectivity for the reaction in three ionic liquids, $[EtNH_3][NO_3]$ (6.7:1), [bmim][BF$_4$] (4.6:1) and [bmmim][BF$_4$] (2.9:1). These compare to 6.7:1 for methanol, 5.2:1 for ethanol, 4.2:1 for acetone and 2.9:1 for diethyl ether, under similar conditions.[7] Clearly the ionic liquids show a spread of behaviours that is just as great as that seen for molecular solvents. It has previously been shown[10] that all three of the ring protons in *N*,*N*-disubstituted imidazolium cations can hydrogen bond to anions and that the strongest of these interactions occurs at the 2-position of the ring. With its N-H protons, ethyl ammonium nitrate is expected to have even stronger interactions. Hence, the selectivity of the reaction appears to follow degree of cation-anion hydrogen bonding. This would seem to support an "internal pressure" explanation for the differences in the observed selectivities.

Table I. The Diels-Alder addition of methyl acrylate and cyclopentadiene in three ionic liquids.

Ionic Liquid	*endo/exo* ratio
[bmmim][BF_4][a]	2.9:1
[bmim][BF_4][b]	4.6:1
[$EtNH_3$][NO_3][3]	6.7:1

[a] $[bmim]^+$ is the 1-butyl-3-methylimidazolium cation; [b] $[bmmim]^+$ is the 1-butyl-2,3-dimethylimidazolium cation

To investigate this phenomenon further, we compared the *endo/exo* ratio for the reaction in 5 ionic liquids with a common cation but with different anions (Table II). Since the cation remains the same in all of these liquids, its ability to hydrogen bond donate remains constant. However, the ability of the anion to hydrogen bond accept changes with the different ionic liquids. For the $[bmim]^+$ cation, the ^1H nmr chemical shift of the proton of the 2-position of the imidazolium ring (H^2) in a neat ionic liquid can be used as a measure of the degree of hydrogen bonding between the cation and anion.[10] The greater the chemical shift then the greater the hydrogen bonding.[10]

Table II. The Diels-Alder addition of methyl acrylate and cyclopentadiene *endo/exo* ratio as a function of hydrogen bonding of $[bmim]^+$ to the anions.

Ionic Liquid	*endo:exo* ratio	$\delta(H^2)$/ppm	E_T^N
[bmim][CH_3SO_3]	3.8:1	8.54	0.62
[bmim][TfO]	4.5:1	7.86	0.64
[bmim][BF_4]	4.6:1	7.63	0.67
[bmim][ClO_4]	4.7:1	7.84	0.65
[bmim][PF_6]	4.8:1	7.34	0.67

If the explanation of the difference in the *endo/exo* ratios in different ionic liquids was that hydrogen-bonding interactions between the cation and

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anion of the ionic liquids lead to increased solvophobic interactions and hence internal pressure, it would be expected that as the chemical shift of H^2 increased the *endo/exo* ration would increase. This is clearly not the case, indeed the opposite is true (Table II). Hence another explanation is required.

It is well known that Lewis acid catalysts can have a dramatic effect on both the rates and selectivities of Diels-Alder reactions.[9] This occurs by the Lewis acid coordinating to the carbonyl oxygen of the methyl acrylate. This leads to an enhancement of the effect of the electron withdrawing group, further polarisation of the double bond of the dienophile and better HOMO-LUMO overlap in the activated complex of the reaction.

It has been shown that in a Lewis basic [emim]Cl-$AlCl_3$ (48 mol % $AlCl_3$) ionic liquid the *endo/exo* ratio of the addition of methyl acrylate to cyclopentadiene is 5.25:1 under conditions similar to ours.[5] By changing to an acidic regime the (51 mol % $AlCl_3$) ratio leaps to 19:1.[5] We have ourselves used scandium(III) triflate as a Lewis acid catalyst in a [bmim][TfO] ionic liquid and achieve an *endo/exo* ratio of 16.5:1. This led us to investigate the possibility that a similar interaction was occurring in the ionic liquids themselves (Figure 1). Indeed, it has been suggested that, in Diels-Alder reactions in dichloromethane with added imidazolium salts, their role is to act as Lewis acid catalysts.[11]

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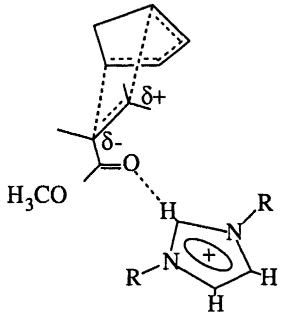

Figure 1. The hydrogen bond (Lewis acid) interaction of an imidazolium cation with the carbonyl oxygen of methyl acrylate in the activated complex of the Diels-Alder reaction.

Table II also shows the normalized Reichardt's E_T^N polarity scale values for the ionic liquids. In ionic liquids this scale is dominated by the ability of the solvent to stabilize the ground state of the dye through hydrogen bonding to the phenoxide site of the dye,[12] giving a measurement of the liquid's ability to hydrogen bond to a solute. It can be seen that the *endo/exo* ratio correlates well with the E_T^N value of the ionic liquid, and hence the ability of the liquid to hydrogen bond to a solute. If the cation has been unchanged, its ability to act as a hydrogen-bond donor has been unchanged, so why is an effect seen? This can be explained by the observation that the selectivity of the reaction decreases as the cation-anion hydrogen bonding increases. The interaction with the methyl acrylate is *via* a hydrogen bond between the cation and the carbonyl oxygen of the electron withdrawing group. Clearly there is a competition between the anion and the solute for the proton. Although the individual hydrogen bonds to the cations would be expected to be much weaker than that to the methyl acrylate, the anions are available in much higher concentrations. Hence, the *endo/exo* ratio and associated acceleration of the Diels-Alder addition of cyclopentadiene and methyl acrylate in ionic liquids is controlled by the ability of the liquid to act as a hydrogen-bond donor (cation effect) moderated by its hydrogen-bond acceptor ability (anion effect). This may be described in terms of two competing equilibria. The cation can hydrogen bond to the anion:

$$[\mathrm{bmim}]^+ + \mathrm{A}^- \rightleftharpoons [\mathrm{bmim}]...\mathrm{A}$$

$$K'_{\mathrm{eqm}} = \frac{[[\mathrm{bmim}]...\mathrm{A}]}{[[\mathrm{bmim}]^+][\mathrm{A}^-]}$$

The cation can hydrogen bond to the methyl acrylate:

$$[\mathrm{bmim}]^+ + \mathrm{MA} \rightleftharpoons [\mathrm{bmim}]...\mathrm{MA}$$

$$K'_{\mathrm{eqm}} = \frac{[[\mathrm{bmim}]...\mathrm{MA}]}{[[\mathrm{bmim}]^+][\mathrm{MA}]}$$

It can be clearly seen that the concentration of the hydrogen bonded cation-methylacrylate adduct is inversely proportional to the equilibrium constant for the formation of the cation-anion hydrogen bonded adduct (K'_{eqm}).

The room-temperature ionic liquids give substantial *endo* selectivity enhancements, and associated rate enhancements, in the reaction of cyclopentadiene with methyl acrylate when compared to non-polar solvents. Hence, they offer the potential to be useful solvents for Diels-Alder cycloadditions, and related reactions, particularly for moisture and oxygen sensitive reagents. The greatest selectivities will be observed in ionic liquids with the strongest hydrogen-bond donor capacity coupled with the weakest hydrogen-bond acceptor ability. Further to this we can predict that this behaviour will be general and in any reaction where a reactive centre is activated by a neighbouring electron withdrawing group such an ionic liquid will further enhance its reactivity. We are continuing to investigate these propositions.

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Chapter 20

Working Salts: Syntheses and Uses of Ionic Liquids Containing Functionalized Ions

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The immobilization of specific chemical entities on supporting materials is a technology of phenomenal scope and importance (*1-3*). Long used industrially as a method for facilitating the recovery of precious metal catalysts, reagent immobilization plays central roles as well in areas as diverse as water purification and solid-phase combinatorial synthesis.

A basic rationale for using this technology is the ease of separation that is provided by the immobilization of a reagent or catalyst on a heterogeneous support. In petroleum cracking, this takes the form of a metal salt adsorbed onto a mineral support. Such catalyst-support systems are easily separated by physical means from gaseous or liquid products. In biochemistry, the immobilization of an amino acid on plastic beads allows additional amino acids to be added to the first in a sequence specific manner. The desired polypeptide can subsequently be removed at the completion of the synthesis in an environment free of byproducts or unreacted reagents.

The increased ease of separation notwithstanding, the immobilization of catalysts and substrates on solid supports creates other problems (*4*). For example, in the particular case of heterogeneous catalysts, low specificity, high reaction temperatures and temperamental kinetics characterize many systems. These problems stem chiefly from the encumbered access to the surface-bound catalyst that is presented to the substrate molecule. The simultaneous need for the diffusion of fresh substrate to and product away from the solid surface become mutually hindering processes. Moreover, the number of directions in which the substrate may approach the catalytic site is sharply curtailed by the massive bulk of the support.

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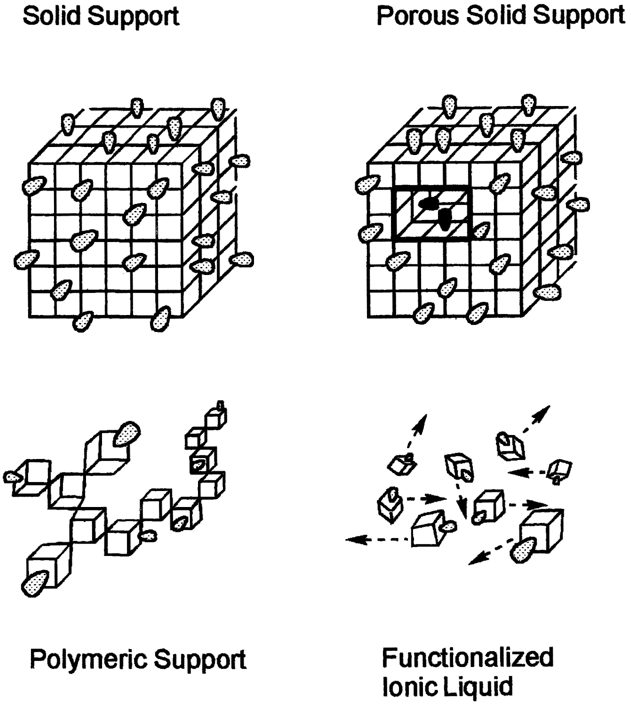

Figure 1. Reagent and catalyst heterogeneous type support systems.

Attempts to circumvent these problems have largely focused on dispersing the supported reagents onto solids that have higher surface areas (e.g., porous solids or polymers), though other approaches such as using reagents "immobilized" in aqueous and fluorous phase liquid supports are also being used (*5*). While these systems offer some clear advantages over classical solid supports (Figure 1), they still do not constitute ideal systems. An arguably better system would be one in which each molecular unit of the supporting material bore functionality and was itself free to diffuse, while retaining a high degree of phase heterogeneity with other solvents, reagents, *etc.*, allowing easy separation. Moreover, the utility of this liquid supporting medium would be enhanced by a diminished capacity for evaporative loss versus water or fluorocarbons. We are endeavoring to craft "task-specific" ionic liquids for use as just this type of system.

Despite their formal similarity, a key characteristic distinguishes ionic liquids from other molten salts. Specifically, salts categorized as ionic liquids melt at temperatures many hundreds of degrees lower than do typical, wholly inorganic salts such as NaCl (mp = 800°C). Their liquidity at low temperature combined with vanishingly small vapor pressures and a remarkable capacity to solvate an array of organic and inorganic substrates have made ionic liquids materials of intense interest as potentially "green" solvents. As essentially non-evaporable entities, ionic liquids may be suitable for replacing VOCs (volatile organic compounds) in a variety of applications. Given that the annual worldwide use of VOCs has a value of about six billion dollars, their replacement with these non-evaporating solvents could produce a considerable economic and environmental impact (*6*).

Overall, research into ionic liquids has been largely limited to a small number of ion pairings (*7*). The cation of these salts is typically 1-ethyl-3-methyl imidazolium, $[\text{emim}]^+$ or 1-butyl-3-methyl imidazolium, $[\text{4-mim}]^+$. A similarly small family of typical anions, mostly chloroaluminates, fluorophosphate, fluoroborate or bis(trifluoromethyl)sulfonamide, is used as well. By judicious choice of the anion and cation, ionic liquids may be formulated that are immiscible with water, molecular organic solvents, or both (Figure 2).

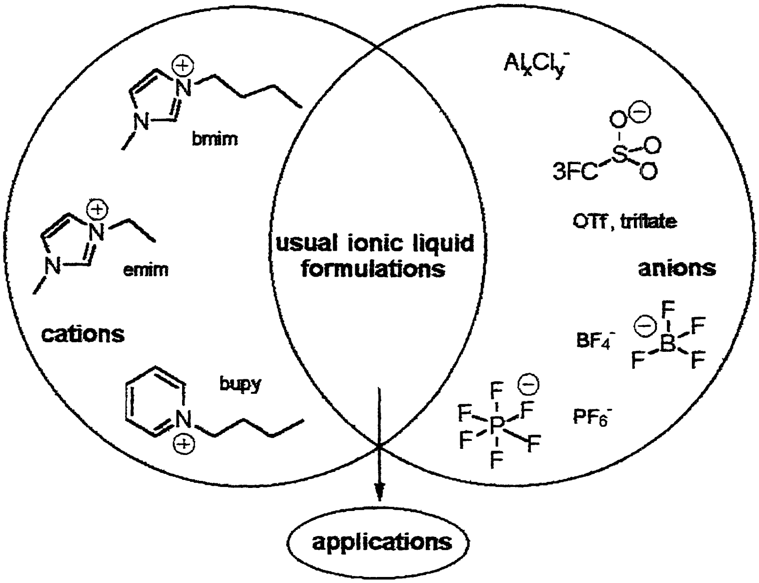

Figure 2. Typical ionic liquid ion pairs.

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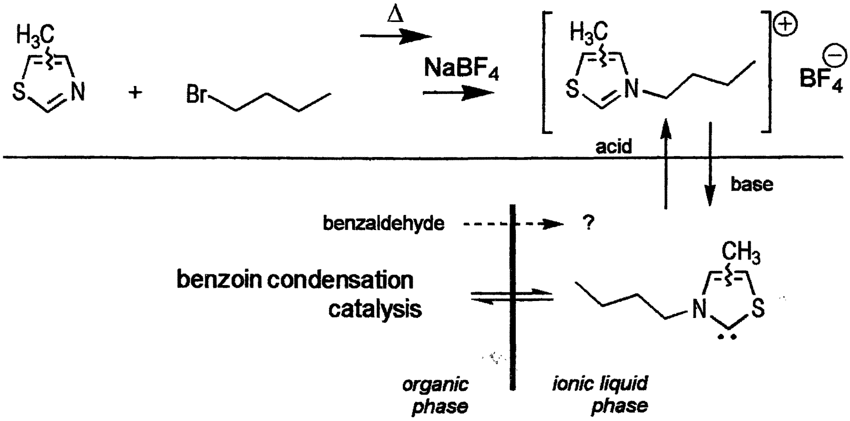
It is the goal of our research to design and synthesize ionic liquids that possess enhanced capacities for interacting with particular types of substrates while retaining control over the IL miscibility with co-solvents. By incorporating a capacity for selective interactions with substrates, we can create task-specific ionic liquids – ionic liquids capable of accomplishing specific tasks ranging from metal extraction from aqueous solutions to the solvation and catalysis of organic reactions. Indeed, by grafting functionality into these salts – ion by ion – and retaining phase heterogeneity with other solvents, we are formally creating the type of improved heterogeneous support systems previously outlined. In this effort, we expect to expand the number of situations where ionic liquids can be utilized in place of organic solvents or solid support systems in synthesis, separations and other applications.

Both the cation and anion of ionic liquids are potential targets for structural and compositional modification. To date, the major focus of our efforts has been on cation modification, though ample opportunities exist for anion modification as well. Conceptually, the ion structures can be regarded as possessing two elements. The first element is a core that bears the ionic charge and serves as the locus for the second element, the substituent groups. The core of the cations may be as simple as a single atom such as N, P or S, as found in ammonium, phosphonium or sulfonium ions, respectively. Alternatively, the core of the ion may be (and more commonly is) a heterocycle such as imidazole or pyridine. Substituents are typically straight-chain alkyl groups, but may in theory incorporate any type of organic group.



Scheme 1. A prototype task-specific ionic liquid (TSIL) system.

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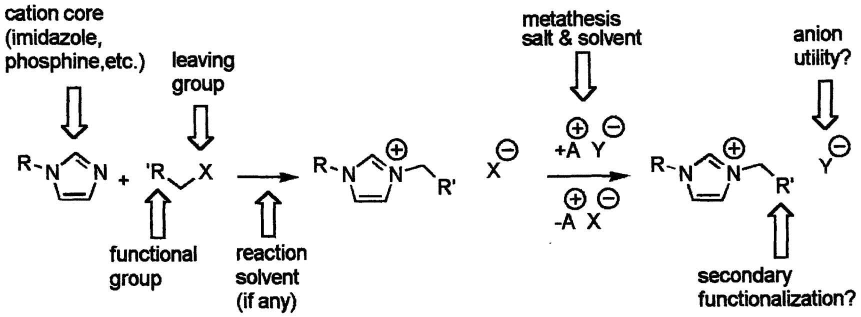
We first demonstrated a capacity for task-specific ionic liquid design and synthesis with the preparation of 3-butyl-4-methyl- and 3-butyl-5-methyl thiazolium salts (*8*). These cations are structural homologs of the [4-mim]$^+$ cation, in which the core of the ion is changed from an imidazole ring to a thiazole ring. Alkylated thiazolium cations such as these are known to undergo facile deprotonation at the ring C(2) position, generating a reactive intermediate with two limiting canonical structures, that of a carbene or an ylide (Scheme 1). These reactive intermediates are known to catalyze a C-C bond forming reaction between aldehydes known as an "acyloin condensation." Previously characterized thiazolium salts, featuring halide anions, were relatively high melting solids. We found that by the simple replacement of iodide by tetrafluoroborate, we could isolate these salts as room-temperature liquids. More importantly, as liquids both demonstrated the capacity to dissolve a typical aldehyde, benzaldehyde, and when treated with a small amount of base, each acts as both the solvent and catalyst source for the condensation of the dissolved benzaldehyde to benzoin (Scheme 1).

Frequently, the incorporation of functionality into an ion slated for use in formulating an ionic liquid is a multi-step process. Consequently, a number of issues must be considered in planning the synthesis of the ion. As illustrated in Scheme 2, the first issue is the choice of cationic core. For example, salts of phosphonium cations appear to generally exhibit the greatest thermal stability, but also generally possess higher melting points than salts of other cations. Thus, if the desired ionic liquid is to be used in a process that is conducted at 0°C, choosing to build the cation core around a phosphonium ion might not be the most useful approach. If the ionic liquid is to be used in a metal catalyzed reaction, the use of an imidazolium based ionic liquid might be critical, especially in light of the possible involvement in some such reactions of imidazolidene carbenes originating with the IL solvent.


cation core (imidazole, phosphine,etc.)
leaving group
functional group
reaction solvent (if any)
metathesis salt & solvent
+A Y
-A X
anion utility?
secondary functionalization?
R
N
R'
X
Y

Scheme 2. General plan for functionalized cation synthesis.

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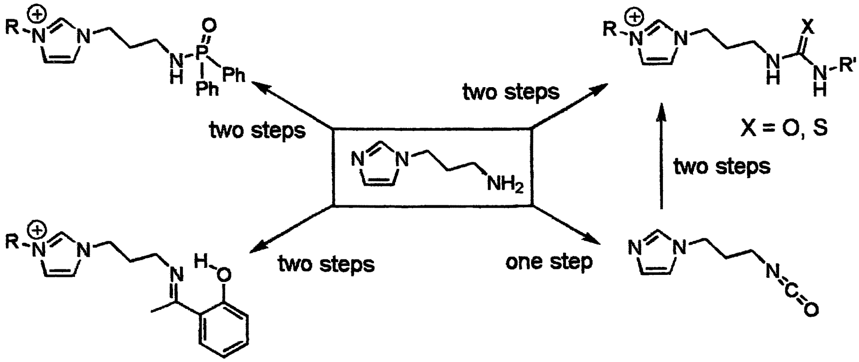
The second element of general importance in the creation of the task-specific ionic liquid is the source of the functional group that is to be incorporated. In the thiazolium based ionic liquids described earlier, this consideration was coincident with the choice of the cationic core. In our hands, however, it is more common to graft functionality onto the cation core. Doing so thus requires the chemist to identify a substrate that contains two functional groups with different reactivity, one which allows the attachment of the substrate to the core, and the other of which either is the functional group of interest or is modifiable to the group of interest. We have generally used functionalized alkyl halides in this capacity, although the triflate esters of functionalized alcohols work as well.

The choice of reaction solvent is also of concern in the synthesis of new ionic liquids. In our hands, toluene and acetonitrile have proven to be the most versatile, our choice in any given synthesis being dictated by the relative solubility of the starting materials. This element of the synthesis of ionic liquids is decidedly the least "green." Significantly, recent developments in the area of the solventless synthesis of ionic liquids promise to improve this situation (*9*).

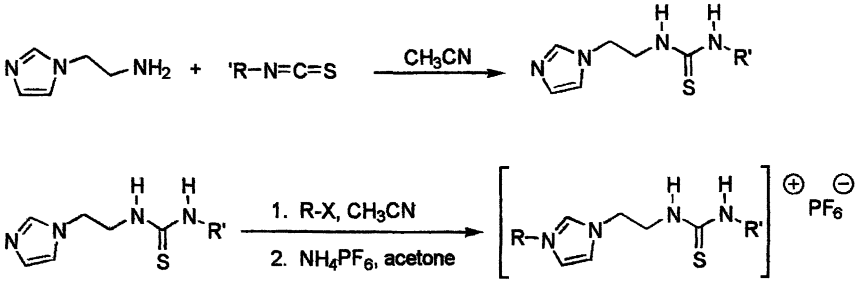
The choice of the anion that is to ultimately be an element of the ionic liquid is of key significance. Perhaps more so than any other single factor, it appears that the anion of the ionic liquid exercises a significant degree of control over the molecular solvents (water, ether, etc.) with which the ionic liquid will form two-phase systems. For example, nitrate salts are typically water miscible and those of hexafluorophosphate are not; those of tetrafluoroborate may or may not be, depending on the nature of the cation. Certain anions such as hexafluorophosphate are subject to hydrolysis at higher temperatures, while those such as bis(trifluoromethane)sulfonate are not, but are extremely expensive. Additionally, the cation of the salt used to perform any anion metathesis is important. While salts of potassium, sodium and silver are routinely used for this purpose, we have found the use of ammonium salts in acetone to be the most convenient. All of these factors must be weighed when making a decision about the appropriate choice of anion for an IL formulation.

As mentioned, though our first endeavor in the preparation of a task-specific ionic liquid featured the incorporation of function at the cation core, most of our subsequent efforts have focused on the incorporation of functionality into a branch appended to the core. While a number of the task-specific ionic liquids that we have prepared have been built-up from 1-methyl and 1-butyl imidazole, many of our more recently prepared functionalized cations have been constructed upon a relatively inexpensive, commercially available starting "scaffold," 1-(3-aminopropyl) imidazole. The appended amino group in this material is a versatile reactive site that lends itself to conversion into a variety of derivative functionalities (Scheme 3).



Scheme 3. Representative cations derived from 1-(3-aminopropyl) imidazole.

Reaction of 1-(3-aminopropyl) imidazole with isocyanates and isothiocyanates gives urea and thiourea derivatives, respectively (Scheme 4). These elaborated imidazoles are then ring quaternized by reaction with alkyl iodides to produce the corresponding N(3)-alkylimidazolium salts. However, the alkylation reactions must be conducted within relatively narrow temperature and solvent parameters to accomplish the alkylation at the imidazole nitrogen and minimize the formation of the undesired alkyl isourea or alkyl isothiourea by alkylation at C=O or C=S. Similar care must be exercised in the synthesis of IL cations with appended acetamide and formamide groups.



Scheme 4. Synthetic plan for Hg^{2+} and Cd^{2+} binding TSIL.

A variation on this overall synthetic approach allows the formation of related IL – ureas by first converting 1-(3-aminopropyl) imidazole into an isocyanate, followed by its reaction with an amine and alkylating agent. The latter approach has been used successfully to append both amino acids and nucleic acids onto the imidazolium cation skeleton.

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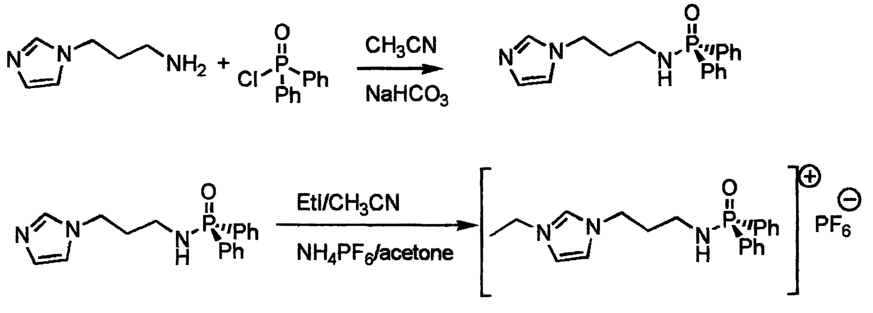
The movement of hydrated metal ions from an aqueous phase into a conventional ionic liquid second phase is decidedly unfavorable. Indeed, partition coefficients for several different metal ions in water - [4-mim]PF_6 biphasic systems are 10^{-1} or less. We reasoned that task-specific ionic liquids with appropriately chosen Lewis base appendages might be used to increase the movement of metal ions into an ionic liquid phase. Accordingly, we have used several of the urea and thiourea ionic liquids as extractants of heavy metals, especially Hg^{2+} and Cd^{2+}, from an aqueous co-phase, with dramatic results (*10*). Depending upon the pH of the aqueous phase, partition of these metals into a mixed system of urea or thiourea TSIL and [4-mim]PF_6 resulted in partition coefficients of up to 10^3 for movement of the metal ions into the IL phase from water.

The removal of actinides from aqueous waste is a major technical challenge to be addressed in the remediation of wastewater at nuclear processing sites such as that at Hanford, Washington. A major consideration in the application of ionic liquids to this task are the poor distribution coefficients of the aquated metal ions into an IL phase. Consequently, ligands are added to the system to complex the metal ion and render it more soluble in the ionic liquid. The resulting complexes may still, however, retain a high degree of water solubility. We reasoned that the approach we utilized previously to facilitate the sequestration of Hg^{2+} and Cd^{2+} from water - the anchoring of the complex into the IL phase by appending the ligand to an "IL-like" ion - might similarly prove useful in the removal of actinides from water.



Scheme 5. Synthetic plan for actinide binding TSIL.

Among the most avidly binding ligand types for actinide ions are phosphoramides and phosphine oxides (*11*). The former are readily synthesized via reaction of phosphorous (V) oxyhalides and primary or secondary amines. Using just such an approach, 1-(3-aminopropyl) imidazole was allowed to react with commercially available $(C_6H_5)_2POCl_2$ in dichloromethane. After isolation, the resulting phosphoramide was then quaternized at the imidazole N(3) position by reaction with ethyl iodide (Scheme 5). The product salt, a viscous oil, mixes readily with more conventional ionic liquids such as [6-mim]PF_6, yielding a more tractable material. Agitation of this liquid with a brilliant yellow aqueous solution of uranyl acetate results in the immediate and dramatic movement of the yellow color into the ionic liquid. Similar contact between aqueous uranyl acetate and pure [6-mim]PF_6 results in no apparent movement of color into the IL phase. Detailed measurements of the capacity of ionic liquid mixtures incorporating the phosphoramide-appended IL to remove actinides from aqueous solution are in progress with Am^{3+}, UO_2^{2+} and Pu^{4+}. Preliminary results suggest partition coefficients for these metals with the phosphoramide TSIL are in the same range as those found for Hg^{2+} and Cd^{2+} with the urea and thiourea IL.

We have taken a different synthetic approach for the preparation of a second class of ionic liquids / IL additives designed for the sequestration of actinides. These simple, hybrid phosphonium ion - phosphine oxide species are easily prepared beginning with a commercially available starting material, 1,4-bis(diphenylphosphino) butane. The bisphosphine is reacted in a 1:1 stoichiometry with an alkylating agent such as methyl iodide or methyl triflate, producing the expected statistical distribution of mono- and diphosphonium ions, as well as unreacted starting material. Solubility differences between these products facilitate their relatively straightforward separation. After anion exchange (in the case of iodide salts), the monophosphonium salt is dissolved in dichloromethane and stirred together with 30% aqueous hydrogen peroxide. Decantation of the organic layer followed by solvent evaporation leaves a white residue of phosphonium - phosphine oxide salt. Though solids at room temperature, these salts are soluble in conventional ionic liquids. And, like solutions of phosphoramide IL and [6-mim]PF_6 mentioned earlier (*vide supra*), solutions of the hybrid phosphonium-phosphine oxide ILs in the latter also result in the apparent partition of uranyl cation into the ionic liquid phase.

Task-specific ionic liquids designed for the binding of metal ions need not be only monodentate in nature. Taking a hint from classical coordination chemistry, we have recently prepared our first bidentate TSIL. This species is readily prepared in a two step process. First, 1-(3-aminopropyl) imidazole is condensed under Dean-Stark conditions with 2-salicylaldehyde, giving the corresponding Schiff base. This species is readily alkylated in acetonitrile to form the imidazolium salt. Mixed as the PF_6^- salt in a 1:1 (v/v) fashion with [6-mim]PF_6, this new TSIL quickly decolorizes green, aqueous solutions containing Ni^{2+} with which it is placed into contact, the color moving completely into the IL phase (Scheme 6). We are currently working to isolate and characterize the putative Ni – TSIL complex.

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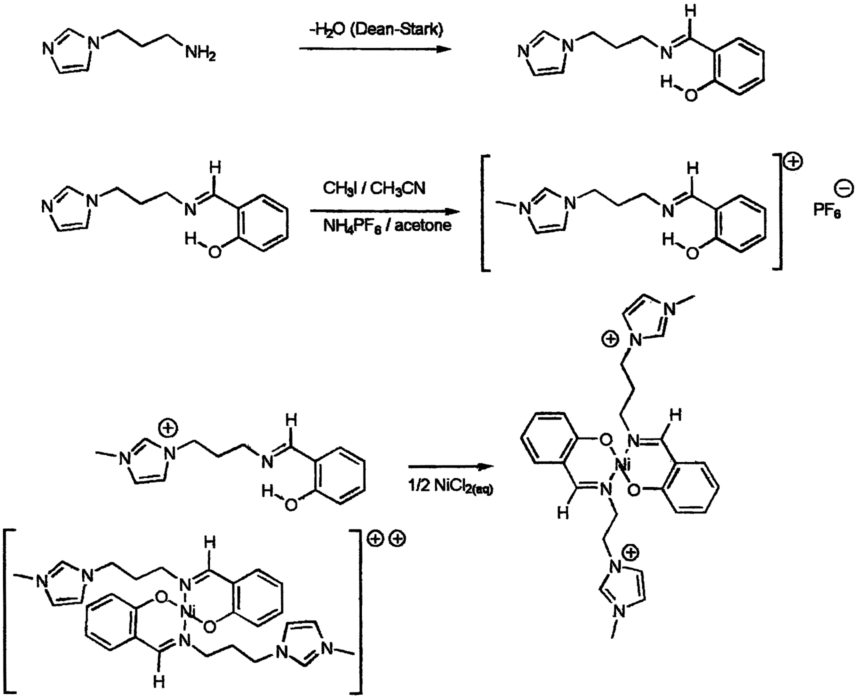

Scheme 6. Synthetic scheme and proposed mode of binding of Ni^{2+} by a bidentate Schiff base TSIL.

The utilization of functionality in ionic liquid formulation need not be limited to effecting the solubilization of metals in ionic liquid phases. For example, we recently developed a family of ionic liquids that contain imidazolium cations with long, appended fluorous tails. While the solubility of these species in conventional ionic liquids is rather limited (saturation concentrations of about 5 mM), the TSIL apparently form fluorous micelles in the latter. Thus, when a conventional ionic liquid doped with the fluorous TSIL is mixed with perfluorocarbons, extremely stable emulsions can be formed (Figure 3). These may be of use in developing fluorous – ionic liquid two-phase reaction systems (*12*).

While the majority of our focus has concerned the modification of ionic liquid cations, we have also begun to probe the use of a rather conceptually unorthodox anion class, the sheet layers of aluminosilicate clays. Ion-exchangeable clays are a class of naturally occurring materials that consist of sheet-like layers of aluminum and silicon atoms bridged and terminated by oxygen atoms and hydroxyl groups. The isomorphous replacement of sheet

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metals by ions such as Fe^{3+} gives rise to permanent charges on the sheet structures. In the natural systems, these negative charge on these structures are offset by alkali metal or alkaline earth cations that are interspersed between the sheet structures in areas referred to as galleries (*13*).

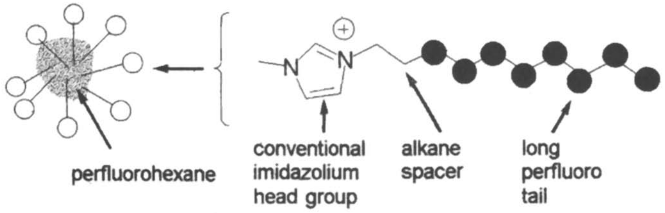

Figure 3. Micelle formation by fluorous ionic liquids.

The replacement of gallery cations by alkyl ammonium and alkyl pyridinium salts is well precedented. The designed ion exchange of these cations by select organic cations has given rise to tailored clay materials that can be swelled by organic solvents. With properly chosen solvents, the clay sheets can be sufficiently separated to be considered to be exfoliated. That is, at interlamellar separations of 100 Å or so, the aluminosilicate sheets can be regarded as acting autonomously. This technology has allowed the incorporation of dispersed nanoscale mineral platelets into organic polymers, leading to significant improvements in polymer properties (*14*).

In addition to the one-to-one replacement of gallery cations by cationic organic species, the uptake into clay galleries of alkyl ammonium salts in excess of the ion exchange capacity has been documented (*13*). This phenomenon is of considerable potential relevance to ionic liquids chemistry. Indeed, to the degree that such chemistry occurs in an ionic liquid, the ionic liquid could be regarded as being composed in part of the mineral.

In more practical terms, the environmental fate of ionic liquids is a topic of some considerable importance, but is an issue that has yet to be the subject of much study. Given that clays are a major soil component in many areas, a thorough study of clay interactions with ionic liquids is merited. Too, ionic liquid clay interactions are of potential significance since clays are both "green" and catalytic in many types of organic reactions (*15*).

We have recently determined that clay minerals such as bentonite and montmorillonite undergo complete cation exchange with the common ionic liquid cations $[6\text{-mim}]^+$ and $[4\text{-mim}]^+$. Moreover, the ion-exchanged materials readily take up excesses of these cations when paired with PF_6^-. In preliminary

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powder X-ray diffraction studies, we have observed ionic liquid induced interlayer separations as great as 60 Å. Given this capacity for the uptake of ionic liquids by clay minerals, these materials can be suggested as potential sequestering agents in the event of ionic liquid spills. Moreover, these results suggest that the widespread dispersion of an ionic liquid into the soil at the site of a spill may be retarded in soils with higher ion-exchangeable clay content. Further studies on this point, as well initial studies on the catalysis by clays of organic reactions in ionic liquid solvents are in progress.

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Chapter 21

Gas Solubilities in 1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate

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The solubility of carbon dioxide, ethylene, ethane, and methane in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) at 25°C are reported. This information is important in evaluating ionic liquids as media for reactions involving gases (i.e., C_2H_4), considering the extraction of solutes from ionic liquids by gas stripping or supercritical fluid extraction, and considering the use of ionic liquids for gas separation and purification. Carbon dioxide is quite soluble in [bmim][PF_6], followed by ethylene, ethane and methane.

Here we present preliminary results for the solubility of various gases in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]). Our motivation for measuring gas solubilities is three-fold. First, the solubility of carbon dioxide (CO_2) in ionic liquids is important for evaluating the possibility of using supercritical CO_2 to extract solutes from ionic liquids, as we have proposed previously (1, 2). Second, various researchers have shown that ionic

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

liquids (ILs) are excellent solvents for a wide variety of reactions (3) involving permanent gases, such as hydrogenations and hydroformylations. The solubility of the gas in the IL is likely to be an important, perhaps limiting, factor in these reactions. Finally, we are interested in exploring the possibility of using water stable ILs for performing gas separations.

Supercritical CO_2 Extraction

Our preliminary work (1) showed that is was possible to remove a target specie (e.g., naphthalene) from an IL by extraction with supercritical CO_2. First, we showed that [bmim][PF_6]/CO_2 is a two-phase system at all pressures and temperatures investigated. Significant amounts of CO_2 dissolved in the IL-rich phase (up to a mole fraction of 0.6 at 80 bar), but there was no measurable IL in the CO_2-rich phase. This is the main advantage of supercritical CO_2 extraction to remove solutes from ILs over liquid/liquid extraction. Next we showed that naphthalene could be extracted reproducibly from [bmim][PF_6] with CO_2 at 138 bar and 40°C with recoveries of 94-96%

Subsequently, we have shown that the phase behavior of [bmim][PF_6] with CO_2 is typical of a variety of systems of CO_2 with imidazolium and pyridinium-based ILs (4). As shown in Figure 1, all of the systems are two phase, with significant amounts of CO_2 dissolving in the IL (dashed line) but no measurable IL dissolving in the CO_2 (solid line coincident with right-hand axis).

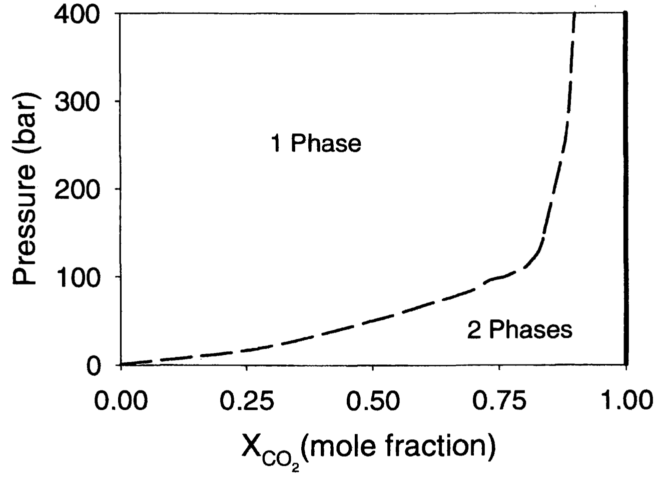

Figure 1. Qualitative phase behavior of an ionic liquid - CO_2 mixture.

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Most recently, we have extracted a wide variety of solutes from [bmim][PF_6] with supercritical CO_2 (2). A sample of these results is shown in Figure 2 for the extraction of a series of aromatic solutes. The percent extracted is shown as a function of the amount of CO_2 used in the extraction. In general, solutes that have a lower solubility in CO_2 are much more difficult to remove. Thus, very polar solid solutes like benzamide, which have relatively low sublimation pressures and very little affinity for CO_2, require substantial amounts of CO_2 to be removed. Nonetheless, all of the compounds can be quantitatively extracted from the IL using CO_2. More importantly, this is done without any cross contamination of CO_2 with the IL.

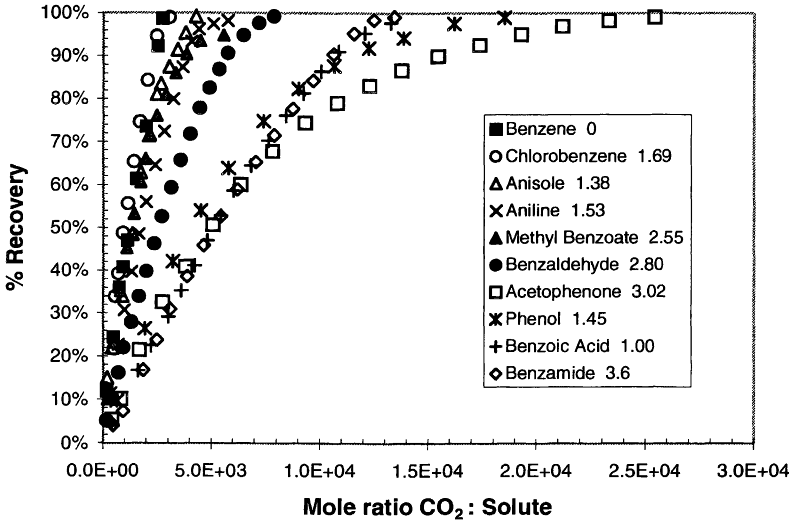

Figure 2. The extraction of various solutes from [bmim][PF_6] with supercritical CO_2 at 138 bar and 40°C. The numbers in the legend are solute dipole moments. (Reproduced from reference 2. Copyright 2001 American Chemical Society.)

Thus, we have shown that CO_2 can completely separate a wide variety of organic solutes from an IL without any contamination of the extract with the IL. CO_2 dissolves in the IL liquid phase, yet the IL does not dissolve in the CO_2, allowing recovery of products in pure form. The key to this process is the phase

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behavior of the ILs with CO_2. Thus, we have been interested in obtaining accurate measurements of CO_2 solubility in ILs over a wide range of conditions.

Reactions Involving Gases as Reagents

Numerous researchers have shown that ILs are attractive solvents for a variety of reactions that use gases as reagents. Most numerous are investigations of hydrogenation reactions (5-12). A particular advantage of ILs is that homogeneous catalysts, that can afford greater selectivity than heterogeneous supported catalysts, can be used. Many noble metal salts and complexes are readily soluble in ILs and remain in the IL even after recovery of the products by distillation or extraction. In addition, it has been shown that ILs are excellent media for hydroformylation reactions (13-16), which require equimolar concentrations of hydrogen and carbon monoxide, as well as an alkene (e.g. ethylene). Very few reports of oxidation reactions have appeared (17), perhaps due to complications involving oxidation of the IL itself. Nonetheless, more examples are no doubt likely to appear.

Assuming that clever schemes can be devised to combat mass transfer resistances (that will no doubt be a significant issue for these relatively viscous solvents), the limited factor in using gases for reactions in ILs is likely to be their solubility in the liquids. Thus, understanding what factors control gas solubility in ILs is very important.

Gas Separations

Since ILs are essentially nonvolatile, they may be excellent solvents with which to do gas separations. In its simplest form, gases can be separated by contacting them with an absorption liquid in which one or more of the gases is significantly more soluble than the others. For instance, ethylene glycol is used to remove water from natural gas streams. One disadvantage of conventional absorbers, however, is that the absorption liquid inevitably exhibits some measurable vapor pressure, thus, contaminating the gas stream, at least to some extent. If different gases exhibited different solubilities in an IL, then it could be used to eliminate this liability. Moreover, ILs would be particularly well-suited for supported liquid membranes to be used for gas separation. This is because they would not evaporate into the gas stream, causing deterioration of the membrane, as is the case with all conventional liquid solvents. For a simple solution/diffusion mechanism for gas separation (as opposed to facilitated transport), the two key physical properties for evaluating liquids are gas diffusion coefficients and gas solubilities. Thus, measuring and understanding the solubility of various gases in ILs is vitally important.

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Experimental

The gas solubility measurements reported here were made using a gravimetric microbalance (IGA 003, Hiden Analytical) that is normally used to measure gas adsorption onto solids. However, since the ILs are nonvolatile they could be used with this apparatus. The microbalance consists of a sample pan and counterweight symmetrically configured to minimize buoyancy effects. The balance has a 1 microgram stable resolution. Approximately 75 mg of ionic liquid sample was added to the sample pan and the chamber was sealed. The sample was dried and degassed by first pulling a coarse vacuum on the sample with a diaphragm pump (Vacuubrand MZ 2d) and then fully evacuating the chamber to ca. 10^{-9} bar with a turbomolecular pump (Pfeiffer TMU 064). The sample was heated to about 75 °C during this process with an external furnace (SFL TF 1042). This activation period typically took between four and eight hours, during which time the sample mass slowly decreased as residual water and gases were driven off. Once the mass had stabilized for 30 minutes, the sample was considered pure, and the absorption measurements were initiated. A schematic of the apparatus is shown in Figure 3, which details the microbalance section, the series of mass flow controllers and the gas cylinders used.

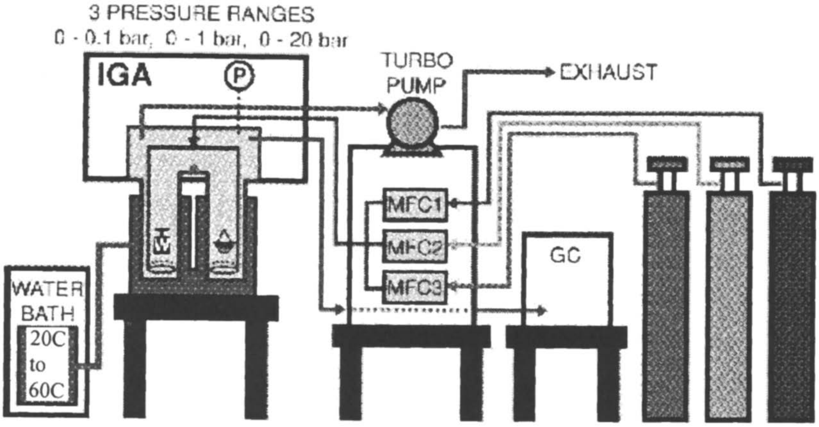

Figure 3. Schematic of gas solubility measurement apparatus.

The furnace was removed and replaced by a water jacket connected to a constant temperature bath (Neslab RTE-111). The sample temperature was monitored with a type K platinum thermocouple placed inside the sample chamber and automatically maintained to within 0.1 °C of the setpoint via the IGA software. Once the desired temperature of the sample was reached, gas was introduced into the sample chamber through a leak valve until a predetermined pressure was reached. The IGA software maintains the pressure to within 0.06% of the setpoint through control of the leak valve and exhaust valve. As the gas entered the chamber, the sample mass increased as gas absorbed into the sample. The weight change was monitored until the mass did not change significantly for 15 minutes, after which the sample was deemed to have reached equilibrium, thus yielding a single point on the absorption isotherm. This process was repeated through a predetermined set of pressures until the maximum practical operating pressure was reached (about 14 bar). Following this, the process was reversed; the gas pressure above the sample was gradually reduced in a series of small desorption steps, during which the decrease in sample mass was recorded. Upon completion of this process, a complete absorption / desorption isotherm was obtained. The degree of hysteresis between the two isotherm branches gives an indication of the accuracy of each value. After the completion of an absorption / desorption loop, the sample was degassed and the mass compared with the initial mass to confirm that the ionic liquid did not volatilize or decompose during the run. Even after performing multiple absorption / desorption experiments over several weeks, none of the samples exhibited a detectable loss in mass.

Two factors are critical in performing these experiments. First, great care must be taken to account for buoyancy effects in the system, even when a symmetric balance is used. We followed a procedure developed in previous work with this microbalance (18). Second, sufficient time must be allowed for the system to reach equilibrium. The ionic liquid samples used in this study are somewhat viscous, so the diffusion of gas into the liquids can be quite slow. We found that an equilibration time for [bmim][PF_6] of between 90 and 180 minutes was sufficient.

A major advantage of using a microbalance for these measurements is that the weight change can be monitored as a function of time, which allows easy determination of the time necessary for equilibrium to be reached. The assurance of attaining equilibrium is important during the run as well as prior to the run to ensure the sample is sufficiently dried.

The CH_4 and C_2H_6 were from Matheson Gas Products with purities of 99.97% and 99.99+%, respectively. The C_2H_4 was CP grade from Mitler Supply with a purity of 99.5% and the CO_2 was from Scott Specialty Gases with a 99.99% purity. [bmim][PF_6] was from Sachem and had a residual chloride content of less than 3 ppm.

Results and Discussion

The solubility of CO_2, C_2H_4, C_2H_6, and CH_4 were measured in [bmim][PF_6] at 25°C and pressures to 13 bar. The results are shown in Figures 4 and 5, below, where they are plotted both as mole fraction and weight percent.

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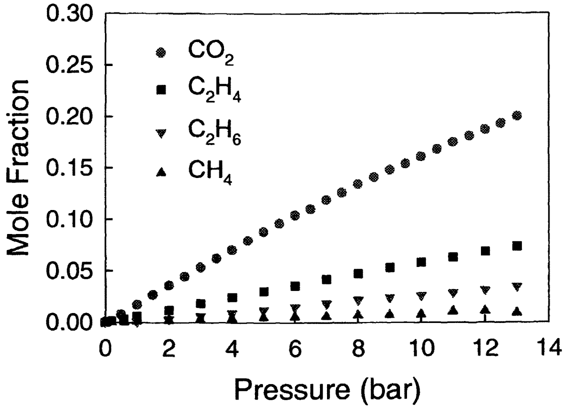

Figure 4. Solubility (in mole fraction) of CO_2, C_2H_4, C_2H_6, and CH_4 in [bmim][PF_6]at 25°C.

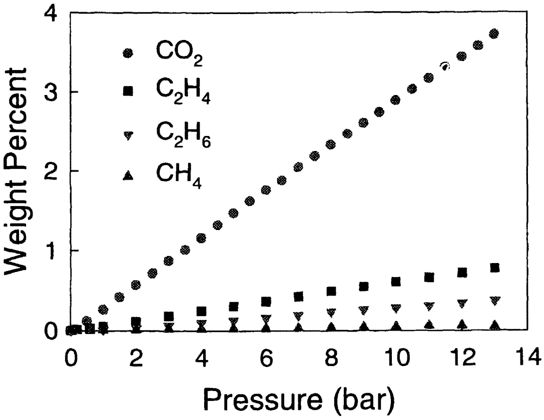

Figure 5. Solubility (in weight percent) of CO_2, C_2H_4, C_2H_6, and CH_4 in [bmim][PF_6]at 25°C.

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The solubility of CO_2 in [bmim][PF_6] is significantly greater than the solubility of any of the other gases. Of the remaining compounds, C_2H_4 is the most soluble, followed by C_2H_6 and C_2H_4. This is true whether considered in terms of mole fraction or weight fraction. The CO_2 solubility values are consistent with our previous measurements (1,4) that were made at higher pressures. Here we show that at just 10 bar pressure the solubility is almost 20 mole %. Conversely, the solubilities of all the other gases at 10 bar are less than 5 mole %. As is clear from Figure 5, the solubility of each of the gases in weight percent is significantly less than the value in mole percent, due to the large molecular weight of the IL compared to the gases.

The simplest way to analyze gas solubility is in terms of a Henry's law constant. The Henry's law constant is defined as:

$$H(\mathrm{T}) = \lim_{x_i \to 0} \frac{f_i^L}{x_i}$$

For vapor/liquid equilibrium of IL/gas mixtures, the equifugacity criterion can be written as:

$$\overset{1}{\cancel{y_i}}\,\overset{1}{\cancel{\phi_i}}\,\mathrm{P} = x_i H$$

Here we assume that the vapor phase is pure gas due to the nonvolatility of the IL, so the mole fraction of gas is unity. Moreover, at the lowest pressures where the Henry's law constant is evaluated there is no need to correct for vapor phase nonidealities with a fugacity coefficient. These simplifications for IL/gas mixtures, as indicated in the equation above, results in the Henry's law constant simply being the slope of the solubility versus pressure plot shown in Figure 4, evaluated in the limit of low solubility.

Thus, we determined the values of the Henry's law constants at the lowest solubilities (i.e., the lowest pressures) where the solubility is a linear function of the pressure. At 25°C, the values obtained were 53.4 ± 0.5 bar for CO_2, 173 ± 18 bar for C_2H_4, 353 ± 36 bar for C_2H_6, and 1690 ± 153 bar for CH_4.

The high solubility of CO_2 confirms our previous investigations that show the viability of supercritical CO_2 extraction of solutes from ILs. Also, the significantly lower solubility of these gases in ILs than the solubility of water vapor (20) suggests that ILs would be particularly well-suited for gas drying applications. Finally, this work suggests that with increasing understanding of the mechanism responsible for gas solubility in ILs, it may be possible to tailor ILs for specific gas separations.

Summary

We have shown how a gravimetric microbalance apparatus, designed for the measurement of gas adsorption onto solids, can be used to accurately measure gas solubility in ionic liquids. The solubility of gases in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) appears to be quite high, especially for CO_2. The Henry's law constants for these gases in [bmim][PF_6] at 25°C are 53.4 ± 0.5 bar for CO_2, 173 ± 18 bar for C_2H_4, 353 ± 36 bar for C_2H_6, and 1690 ± 153 bar for CH_4. The differences in these values suggest that ionic liquids may be excellent solvents with which to perform gas separations.

Acknowledgements

Financial support from the National Science Foundation (grant CTS 99-87627), DuPont, the Clare Booth Luce Fellowship and a National Science Foundation Graduate Research Traineeship Fellowship (grant 9452655) are gratefully acknowledged.

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Chapter 22

Free-Energy Relationships and Solvatochromatic Properties of 1-Alkyl-3-methylimidazolium Ionic Liquids

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Contributions to Kamlett and Taft solvatochromatic parameters for a range of ionic liquids (ILs) have been determined by investigation and correlation of the solvatochromatic responses of the dyes 4-nitroanisole, Reichardt's betaine, and 4-nitrophenol. These studies show that whilst ILs are polar, in terms of descriptors π^*, α, and β, differences in the properties of the ILs derive from variations in their hydrogen-bond donor (HBD) and acceptor (HBA) capability, and perhaps, for a wider set of ILs, in polarity (π^*). In addition, distribution ratios have been determined for a selection of small organic solutes in biphasic systems composed of [1-alkyl-3-methylimidazolium][PF_6] ILs and water and compared to distribution in the 1-octanol-water system. The free energy of transfer of a methylene group has been determined and solute distribution modeled using a Linear Free Energy Relationship (LFER) based upon Abraham's generalized solvation equation.

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

Introduction

Ionic Liquids (ILs) have uses in many areas of chemistry including organic (*1,2*) and inorganic synthesis, biphasic catalysis (*3*), separations processes (*4*) and electrochemistry and electrodeposition. Interest in ILs stems from the unique solvent properties and from the ability to tune the properties of the IL by variation in the structure of the cation and the nature of the anion as indicated in Figure 1. For example, slight alteration in the anion or cation can cause dramatic changes in their physical properties (e.g., density, viscosity, melting point, water miscibility, and refractive index) as described in some recent reviews (*5,6*). Such changes may also be expected to impact chemical properties such as, e.g., polarity, hydrogen bonding ability, and solvent structuredness, each of which will intimately affect their solvent nature. The few studies of their solvent properties published to date, for example using solvatochromatic dyes such as Pyrene (*7*), Nile Red (*8*), and Reichardt's Dye (*8-9*) have tended to suggest that the polarity of various ILs resembles that of the short chain alcohols.

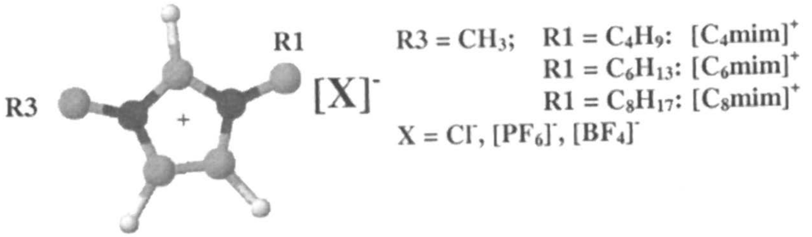
R1
R3
+
$[X]^-$
$R3 = CH_3$; $R1 = C_4H_9$: $[C_4mim]^+$
$R1 = C_6H_{13}$: $[C_6mim]^+$
$R1 = C_8H_{17}$: $[C_8mim]^+$
$X = Cl^-, [PF_6]^-, [BF_4]^-$

Figure 1. Structures of ionic liquids employed in these studies.

Unfortunately for ILs, as with other solvents, the meaning of the term polarity is generally abused, and tends to be used as if in comparison to water and as a synonym for hydrophilicity, however, for the chemist this should not be so. A number of quite distinct interactions govern solvation in any molecular or ionic solvent, including hydrogen bonding, dipolar interactions, and van der Waals forces. This may be illustrated by reference to a generalized model of solvation (*10*) as shown in eq. 1:

$$\text{Solvation} = \text{cavity terms} + \text{H-bonding terms} + \text{polarity terms} \qquad (1)$$

Solvation may be equated to the Gibbs free energy associated with the formation of a cavity in the solvent to accommodate the solute. This is related to the Hildebrand solubility parameter (*10*) and to the cohesive energy density of the

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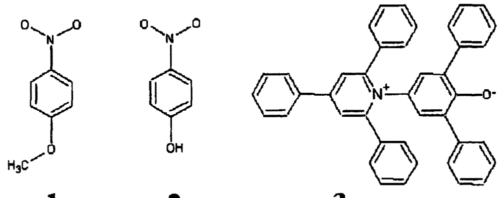
solvent (*10*). Less obviously, in comparison to water, it is also the term for which the description 'hydrophobicity' should be reserved. The other terms describe the free energy associated with solute-solvent interactions. Unfortunately many, indeed most, conventional indicators of apparent solvent polarity do not clearly separate these terms and various empirical correlations have been developed in order to do so (*11*).

The original solvatochromatic Linear Free Energy Relationship (LFER) of Kamlett and Taft (*12*) involved the use of several different probes to arrive at averaged values of the solvent parameters. There is debate over the wisdom of this, some favoring extreme degrees of parameter averaging (*13*), others favoring standardization around a single probe set (*14*). The former approach has the disadvantage that more effort is required to derive parameters in order to characterize a new solvent. Experimental ease combined with a clearly defined meaning is the principal advantage of the latter approach, but this is at the price of some risk of error.

In this study, the behavior of three well-known Kamlett and Taft solvatochromatic dyes have been examined in several ILs based on the 1-alkyl-3-methylimidazolium cation. The indicator dyes (Figure 2) used are 4-nitroanisole (**1**), which is sensitive to solvent dipolarity/polarizability (π^*), 4-nitrophenol (**2**), which is sensitive to solvent H-bond basicity (β), and Reichardt's betaine dye (**3**), which is sensitive to both the H-bond acidity (α) and the polarity of the solvent medium.



1 **2** **3**

Figure 2. Structure of the solvatochromatic probes: 4-nitroanisole (1), 4-nitrophenol (2), and Reichardt's betaine dye (3).

In the second part of this chapter, we report on the distribution of a limited number of small organic solutes between the equilibrium phases of some water immiscible ILs and water. The distribution of these solutes is compared to literature values of their distribution in the 1-octanol-water system. The relative free energy of transfer of a methylene group is estimated from the distribution of a series of aliphatic alcohols and solute distribution is modeled using Abraham's generalized solvation equation (*15*).

Experimental

All aqueous solutions were prepared using deionized water that was purified with a Barnsted deionization system (Dubuque, IA) and polished to 18.3 MΩ•cm. Acid solutions were prepared as molar concentrations by transferring a known amount of material to a volumetric flask and diluting to the specified volume with deionized water. When needed, pH adjustments were made using H_2SO_4 or NaOH.

HPF_6 supplied by Ozark-Mahoning (Tulsa, OK) was used as received. All other chemicals were of reagent grade, obtained from Aldrich (Milwaukee, WI), and used without further purification. Organic molecule partitioning was carried out using ^{14}C-labeled solutes obtained from Sigma (Saint Louis, MO). Additional details of the partitioning procedure and the radiochemicals employed may be found elsewhere (*16*).

The ILs used in this study were synthesized using previously published methods (*4,6*). The water content of each IL was determined using a coulombmetric Aquastar Karl Fischer titrator (EM Science, Gibbstown, NJ) with composite 5 solution as the titrant and anhydrous methanol as the solvent. Each sample was at least 1 g and duplicate measurements were performed on each.

All UV-vis spectra were collected at 25° C using a Cary 3 spectrophotometer (Varian, Sugar Land, TX, USA).

Solvatochromatic Methods

4-Nitroanisole (1)

Absorption spectra of 4-nitroanisole in ILs were taken between 200 and 450 nm. Approximately 3 mg of dye was added to 5 mL of IL, which was then diluted five times in the same ionic liquid so that the absorbance was less than 1.0 in a 2 mm path length quartz cell (Hellma, Forest Hills, NY). Spectroscopy was conducted on ILs of known water content. The π^* values were determined from the wave number (ν) of the longest wavelength absorption band of the 4-nitrophenol dye using eq. 2:

$$\pi^* = 0.427\times(34.12-\nu_{(1)}) \qquad (2)$$

This is the relationship given by Marcus in his review, where ν is the wavelength of the longest wavelength absorption band of the probe in the region around 1000 cm^{-1} (*11*).

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4-Nitrophenol (2)

Absorption spectra of 4-nitrophenol in ILs were taken between 200 and 550 nm as above. Approximately 3 mg of dye was added to 5 mL of IL, which was then diluted five times with the same ionic liquid to be measured so that the absorbance was less than 1.0 in a 2 mm path length quartz cell. Spectra were taken in ILs whose water contents were known. The β values were determined using eq. 3 as given by Marcus (*11*):

$$\beta = 0.346\times(35.045-\nu_{(2)})-0.547\times\pi^{*}-0.12\times\delta \qquad (3)$$

This relationship takes into account that the dye is sensitive to both the polarity and the basicity of the medium. In order to apply this relationship, the magnitude of π^* must be obtained from the absorption spectrum of 4-nitroanisole using eq. 2. The scale is defined from the longest wavelength absorption band of the probe (ν - 1000 cm^{-1}) and δ is a correction factor applicable to aromatic solutes (1.0) and polychlorinated aliphatic solutes (0.5), and which is set to zero for other aliphatic solvents (*11*) (see discussion below).

Reichardt's Betaine Dye (3)

Absorption spectra of Reichardt's betaine dye in ILs were taken between 300 and 800 nm as before. Approximately 3 mg of dye was added to 5 mL of IL which was then diluted five times so that the absorbance was less than 1.0 in a 2 mm path length quartz cell. Spectra were taken in ILs whose water contents were known. The α values were determined using eq. 4:

$$\alpha = 0.0649\times E_t(30)-2.03-0.72\times\pi^{*} \qquad (4)$$

The scaling relationship is again taken from Marcus (*11*) and in this case the $E_t(30)$ value is used as determined from the long wavelength absorption band of the probe from eq. 5:

$$E_t(30) = 28591/\lambda_{max}\ (\text{nm}) \qquad (5)$$

It may be noted that the dye is sensitive to polarity as well as acidity.

^{14}C-Labeled Solute Partitioning

Liquid scintillation analyses of ^{14}C-labeled organics were performed using Ultima Gold scintillation cocktail (Packard Instrument, Downers Grove, IL) and

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a Packard TriCarb 1900 TR Liquid Scintillation Analyzer. The organic solute distribution ratios were determined by mixing 1 mL of IL and 1 mL of an aqueous phase followed by vortexing (2 min) and centrifuging (2000 *g*, 2 min) to equilibrate the phases. Addition of the organic tracer (ca. 0.005 μCi, 5 μL) was followed by two intervals of vortexing and centrifuging to ensure that the phases were fully equilibrated and separated. Each tube was uncapped and 100 μL of each phase was removed for radiometric analysis. Since equal volumes of both phases were removed for analysis, the distribution ratios for the organic solutes were determined as in eq. 6:

$$D = \frac{\text{Activity in the IL lower phase}}{\text{Activity in aqueous upper phase}} \qquad (6)$$

Each experiment was done in duplicate and the results agreed to within 5%. These methods were followed for all the partitioning work (i.e., comparison to 1-octanol-water, determination of free energy of transfer, and the modeling of the linear free energy relationship).

Results

Solvatochromatic Parameters Determined for ILs

Solvatochromatic parameters determined from the ILs studied are tabulated in Table I and compared to other molecular solvents in Table II. Results for each probe are discussed below.

4-Nitroanisole - π^*

4-nitroanisole shows a shift in its longest wavelength absorption band between 450 nm and 200 nm. This compound can be used to directly measure π^*, dipolarity and/or polarizability of the solvent. This probe is insensitive to the hydrogen bond donating (HBD) and hydrogen bond accepting (HBA) properties of the solvent and thus forms the basis of the Kamlett and Taft definition of polarity (π^*) used here.

Table I shows the Kamlett and Taft π^* values obtained. All of the ILs measured showed values between 0.88 and 1.09, with the exceptions of the shortest chain chlorides which have higher values of 1.17 ([C_4mim]Cl) and 1.27 ([C_6mim]Cl). Comparison with data in Table II indicates that the polarity and/or polarizability of the ILs studied is of similar magnitude to that of water, DMSO, nitrobenzene, or *N*-Me-acetamide. In this respect at least they are most unlike the short chain alcohols whose polarity, it may be observed from Table II, is rather lower than that observed for the ILs.

Table I. Solvatochromatic Parameters Obtained for Various ILs

IL	*α*	*β*	*π**	*% water*
[C_4mim]Cl[a]	0.41	0.95	1.17	0.75
[C_6mim]Cl	0.23	0.81	1.27	0.81
[C_8mim]Cl	0.33	0.90	1.09	0.34
[C_4mim][BF_4]	0.73	0.72	1.09	2.07
[C_6mim][BF_4]	0.68	0.54	1.07	4.94
[C_8mim][BF_4]	0.62	0.57	1.04	1.67
[C_4mim][PF_6]	0.77	0.41	0.91	0.21
[C_6mim][PF_6]	0.57	0.58	1.08	0.16
[C_8mim][PF_6]	0.58	0.46	0.88	0.15

[a] Note [C_4mim]Cl is a solid after storage at room temperature and thus was heated, cooled, and used prior to crystallization.

Table II. Solvatochromatic Parameters for Selected Molecular Solvents and ILs

Solvent	*α*	*β*	*π**
Water	1.17	0.47	1.09
Hexane	0.00	0.00	-0.04
Ethanol	0.86	0.75	0.54
n-Butanol	0.84	0.84	0.47
N-Me-acetamide	0.47	0.80	1.01
N-Me-formamide	0.62	0.80	0.90
Formamide	0.71	0.48	0.97
Benzyl alcohol	0.60	0.52	0.98

4-nitrophenol - β

4-nitrophenol shows a shift in its maximum absorption band between 550 nm and 200 nm. This compound can be used to measure β, the hydrogen bond accepting ability of the solvent; a knowledge of π^* is necessary as indicated in eq. 3. However, other probes like tetramethylethylenediaminoacetylacetonato-

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copper(II) perchlorate can be used to measure Donor Numbers (DN) and β without a knowledge of π^* (*9,17*).

The results, shown in Table I, suggest that the nature of the anion is dominant in determining the hydrogen bond accepting ability of ILs. For example increased hydrogen bond accepting ability may be observed (shown by increasing β values) which appears to follow the decreasing hydrophobicity and free energy of hydration of the anion following the order $[PF_6]^- < [BF_4]^- < Cl^-$. It is known from X-ray crystallographic structures that the order of hydrogen bonding ability follows the same order.

It appears that the hydrogen bond accepting ability of the ILs examined cover a wide range, from those of short chain alcohols (ca. 0.8) through to lower β values comparable to, for example, MIBK (0.48 from ref. (*11*)). The ability to tune the H-bond acceptor ability of ILs by selection of different anions is an important feature of their solvent properties and is undoubtedly one reason for the high interest in these materials as media for organic synthesis.

Reichardt's Betaine Dye - α

Reichardt's betaine dye, shows a large shift in its long wavelength absorption band between 800 nm and 450 nm when dissolved in solvents of differing polarity (*8*). As indicated in eq. 4 this compound can be used to measure α, the hydrogen bond donating ability of the solvent, however a knowledge of π^* is necessary.

The results shown in Table I indicate that the anion plays a significant role in determining the H-bond donor ability (acidity) of ILs; although HBD sites in ILs, will be principally the three aromatic protons on the cation! For example, as we increase the hydrophobicity of the anion from Cl^- to $[BF_4]^-$, or to $[PF_6]^-$, we also see an increase in the α values. This is unexpected and may, perhaps, be a result of H-bonding interactions between cation and anion which reduces the apparent acidity of the medium as perceived by the probe. There is less distinction between the α values of the $[BF_4]^-$ and $[PF_6]^-$ anions. On the other hand, the shortest alkyl chain-containing cations appear to show a markedly higher acidity than those with longer chains, which is probably related to 'polar-group dilution' effects associated with increasing the alkyl chain length.

In general terms, the acidity is less than that of water (1.17) and less than most short chain alcohols (ca. 0.8). On the other hand, the acidity is greater than many organic solvents such as aniline (0.26 from ref. (*11*)).

Since, at first glance, there appeared to be some dependence of both α and β values on the nature of the anion, we wondered if the two descriptors could be correlated for this limited set of solvents. Figure 3 shows the relationship between the α and β descriptors for the ILs examined. There does not appear to

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be a direct correlation between the α and β values of these IL. However, it is interesting to note that the more hydrophilic ILs, the chlorides, cluster in an area of the figure defined by high basicity and low acidity. On the other hand, the more hydrophobic ionic liquids tend to cluster in a region defined by lower basicity and higher acidity.

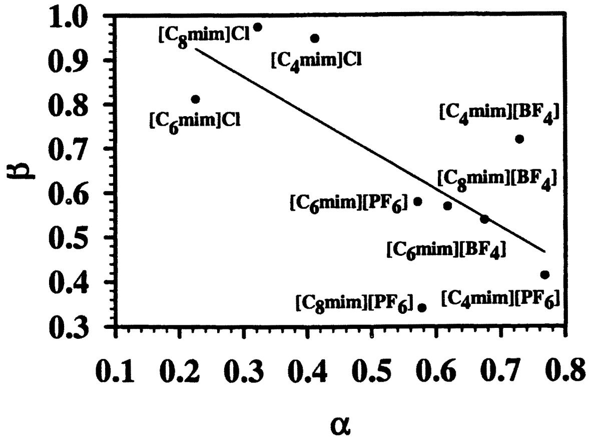

Figure 3. The relationship between α and β parameters measured using solvatochromatic probes for various ILs.

Effect of Water on Solvatochromatic Probe Responses

In order to determine the effect of water on the solvatochromatic probes, an experiment was conducted in which water was systematically added to dried ILs (0.5 to 5 wt%) and the parameters calculated. The results of this experiment are shown in Figure 4 which illustrates that the amount of water present in the ILs has very little effect on the derived solvatochromatic parameters, π^*, α, and β.

The π^* value determined for [C$_8$mim][PF$_6$], 0.88, remains constant at water contents between 0.15 and 2 wt%. However, since the value of π^* measured for the IL differs little from that of pure water, little effect would be observable even if the probe were preferentially solvated by water. The relative constancy of certain values of π^* in Table 1, for example of the BF$_4$ ILs, in the face of wide variation in water content argues against a strong influence of water in the ionic liquid on the measured parameter.

The β values determined for [C$_8$mim]Cl with water content between 0.3 and 5 wt% remain constant at 0.90. In addition, β values for some of the ILs shown in Table I do differ significantly from that of water (0.47), thus an overriding and

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obscuring influence of water on the values obtained seems unlikely. The α values determined for [C_8mim]Cl with water content between 0.3 and 5 wt% held constant at 0.33. In this case, the IL chosen to examine the effect of water differs significantly in determined α value from that of water.

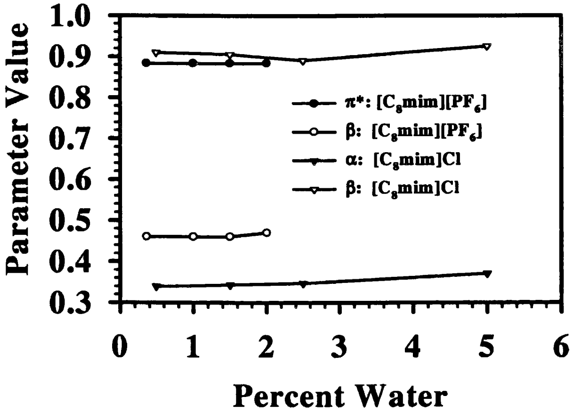

Figure 4. The effect of increasing water content on measured solvatochromatic parameters of ILs.

It is worth noting that although water solvation of the probe microdomain may be an issue due to the presence of more water than solvatochromatic probe in the ILs, it would be anticipated that water would solvate the solvatochromatic probes, 4-nitroanisole and 4-nitrophenol, to approximately the same degree, and thus the effects on π^* and β would be identical. The data here indicates that this is not the case, and over the composition range studied, the solute-solvent interactions in each case occur between the solvatochromic probes and the ILs, rather than with the free water in the system, with little or no effect from the aqueous component composition.

In concentration regimes where water is present as the bulk component (solvated ions), or is at trace levels in the IL, this may not be the case. However, in a recent publication, Bright, *et al.* report that systematically changing the water content of [C_4mim][PF_6], from anhydrous to saturated, had no influence on polarity (*18*). This supports our observations on the aqueous effects on the α, β, and π^* values determined here for [C_8mim]Cl and [C_8mim][PF_6]. Also, in systematic studies of mixed alcohol-water systems from 0 to 1 mole fraction (*19*), the effects of changing solvent composition on solvatochromatic responses of a range of probes were measured (*19*) and showed essentially a linear response as water content was increased through the range of 0 to 0.7 mole

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fraction. That is, the response of the probes seems not to be dominated by preferential solvation by residual water.

Solvent Comparisons

Finally, it is possible to make informed comparisons between ILs and other solvents. Table II shows the solvent properties of a number of molecular solvents. In terms of polarity, the ILs display HBA and HBD characteristics that may reach or exceed the values associated with simple alcohols, but can also be much lower. A meaningful general comparison is therefore elusive in view of this variability. However, the solvents shown in Table II all have solvent property values similar to the currently examined ILs. These include *N*-methyl acetamide and *N*-methyl formamide, which seem to us to stand some degree of practical comparison to the ILs we have examined. Of considerable interest must be the broad range of HBD and HBA values encountered for the relatively small number of ionic liquids examined, serving to emphasize the most exciting properties of this group of solvents, namely the ability to select or fine tune required properties to potential applications. In terms of application in synthetic chemistry, ILs have been used as replacements for polar and dipolar aprotic solvents in, for example, Diels-Alder reactions (*20*), *N-/O*-alkylations (*21,22*), and Heck coupling reactions (*23*).

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Solute Distribution Between IL-Water Phases

The potential role of ILs in liquid-liquid extraction and the role of liquid-liquid extraction in the recovery of products from IL phases have already been alluded to in the literature (*4,24*). We have conducted a study of the partitioning properties of some water immiscible ILs with the aim of highlighting the important solvent properties of ILs in these applications. Such data can only easily be acquired, and are only practically useful, for water immiscible ILs and in this study this was confined to examination of two $[PF_6]^-$ containing ILs.

Various methods may be applied to the study of the solvent properties of liquid-liquid distribution systems. One can apply the Collander relationship (*25*) and make direct comparison to the 1-octanol-water system via log P in which case eq. 7 holds:

$$\log P_1 = a + b(\log P_2) \qquad (7)$$

This assumes that the partition coefficient ($\log P_1$) is a simple linear function of the distribution in the 1-octanol-water ($\log P_2$) system. It is well known that a single linear relationship for all solutes by this method is not possible and applies only to the comparison of functionally similar species. Nevertheless, since log P values are available for such a wide variety of species, its use as a crude estimator of relative system hydrophobicity, just as the use of 1-octanol-water distribution is used as a crude estimator of solute hydrophobicity, is almost inevitable. In Figure 5 we compare solute distribution in the [C$_6$mim]- and [C$_4$mim][PF$_6$]-water biphasic systems to the partition coefficient in the 1-octanol-water system with values of log P taken from the literature. The relationship may be described by eqs. 8 and 9:

$$[C_6mim][PF_6]: \log D = -0.122 + 0.68 \log P \qquad (8)$$

$$[C_4mim][PF_6]: \log D = -0.183 + 0.72 \log P \qquad (9)$$

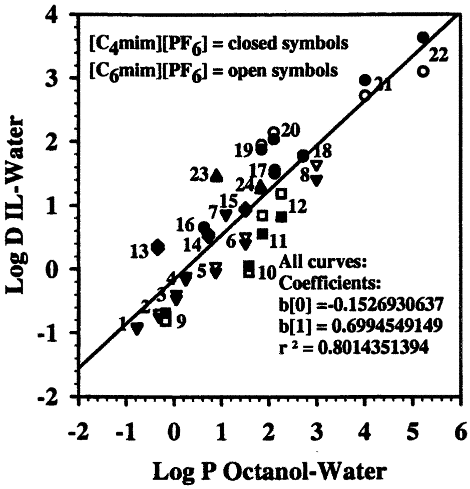

Figure 5. The log of the distribution ratios (D) for a series of small organic molecules [▼ (1) methanol, (2) ethanol, (3) isopropanol, (4) n-propanol, (5) n-butanol, (6) n-pentanol, (7) benzyl alcohol, (8) n-octanol; ■ (9) acetic acid, (10) 4-hydroxybenzoic acid, (11) benzoic acid, (12) p-toluic acid; ◆ (13) acetonitrile, (14) ethyl acetate, (15) methyl iodide; ● (16) benzamide, (17) benzene, (18) toluene, (19) nitrobenzene, (20) anisole, (21) 1,2,4-trichlorobenzene, (22) 4,4-dichlorobiphenyl; ▲ (23) aniline, (24) p-chloroaniline] in IL-water biphasic systems formed with [C$_4$mim][PF$_6$] (closed symbols) or [C$_6$mim][PF$_6$] (opened symbols) vs. log 1-octanol-water partition coefficient (P).

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From eq. 7, log P_0 (defined as the value of log P_2 when log P_1 is zero) may be equated to –a/b (*26*). For the two systems examined, log P_0 has values of 0.18 ($[C_6mim][PF_6]$) and 0.25 ($[C_4mim][PF_6]$). Therefore, solutes having log P greater than log P_0 will prefer the IL phases and vice versa. This provides a useful rule of thumb with which to begin thinking about solvent extraction applications. Nevertheless, it is clear from Figure 5 that the spread of values about the regression line comparing IL-water to 1-octanol-water partitioning means that the description of solute distribution in these simple terms is far from complete. Prediction of solute distribution from log P values will at best be approximate.

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Free Energy of Transfer Relationships

Another approach to solvent property characterization that may easily be derived, involves the determination of the free energy of transfer of a methylene group. This is most easily determined from the distribution of a homologous series of solutes differing by one or more methylene groups and it is common to use the *n*-alcohols in this context.

Typical data relating to *n*-alcohol distribution in the current IL systems is shown in Figure 6. From the slope of the distribution ratios of a series of alcohols versus the number of carbon atoms present, the free energy of transfer of a methylene group may be derived (*27-29*). The results show that the free energy of transfer of a methylene group ($[C_4mim][PF_6]$: $-\Delta G_{CH2} = 0.45$ kcal/mol; $[C_6mim][PF_6]$: $-\Delta G_{CH2} = 0.50$ kcal/mol) is similar to that of MEK. Data for ΔG_{CH2}, the relative degree of hydrophobicity, for these two water immiscible ILs in comparison to some common organic solvents (*30*) are given in Table III.

Table III. Free Energy of Transfer of a Methylene Group between the Phases of Various Aqueous-Organic Biphases

System	*$-\Delta G_{CH2}$ (kcal/mol)*	*System*	*$-\Delta G_{CH2}$ (kcal/mol)*
$[C_4mim][PF_6]$	0.45	Diethylether	0.73
$[C_6mim][PF_6]$	0.50	MIBK	0.72
Hexane	1.10	Xylene	0.64
Chloroform	0.85	Octane	0.77
Benzene	0.84	*n*-Butanol	0.54
Octanol	0.73	MEK	0.43

The value of $-\Delta G_{CH2}$ is relatively small, this may be interpreted as meaning that the cohesiveness of the IL phases is rather greater than that typical of molecular solvents when compared to the cohesivity of water through the process of partition. Greater cohesivity is also implied by their low volatility. On the other hand, it could simply reflect the relatively high equilibrium water content during the partitioning process resulting in the relative cohesive properties of the two phases coming closer to one another.

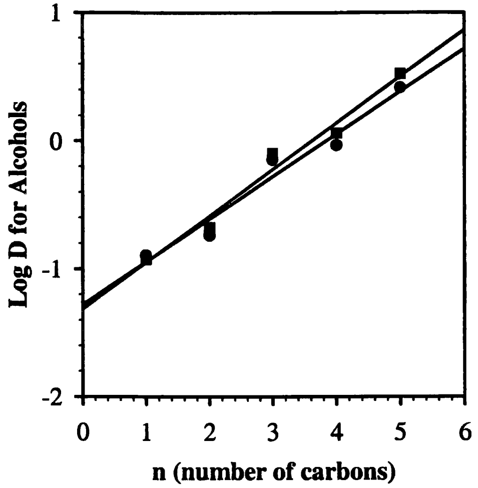

Figure 6. The log of the distribution ratios (D) of a series of aliphatic alcohols (methanol, ethanol, n-propanol, n-butanol, n-pentanol) in IL-water biphasic systems formed with [C_4mim][PF_6] (●) or [C_6mim][PF_6] (■) as a function of the number of carbons in the n-alkyl-chain of the alcohols partitioned.

Organic Solute Distribution Ratios

The distribution ratios of a variety of small organic solutes between the IL ([C_4mim][PF_6] or [C_6mim][PF_6])-water biphasic systems are shown in Figures 7 and 8. The distribution ratios were determined for the neutral form of the solutes (i.e., in conditions under which the solutes were undissociated by manipulation of the aqueous phase pH). Abraham's generalized solvation equation applied to partitioning takes the form of eq. 10:

$$\log P = c + rR_2 + s\pi_2^H + a\Sigma\alpha_2^H + b\Sigma\beta_2^H + vV_x \qquad (10)$$

where P is the partition coefficient and c is a constant. The terms r, s, a, b, and v are coefficients which relate the solute descriptors (*31,32*) to the measured property through a multiple regression of the data on partitioned solutes. The descriptors are: R_2, the molar refractivity of the solute which is considered to encapsulate the contribution to partition due to π- and nonbonding-electron

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interactions, π_2^H describes the solute's tendency to interact through polar/dipolar interactions, $\Sigma\alpha_2^H$, encapsulates the H-bond donor acidity of the solute, $\Sigma\beta_2^H$ considers the H-bond acceptor basicity of the solute, and V_x is the McGowan volume of the solute (*33,34*).

The scaling of the descriptors, at least for small molecules, allows comparison of different solvent-solvent (including solvent-water) partitioning systems through the relative magnitude of the coefficients. The coefficients thus express the relative magnitude of the particular aspect of the interaction between solute and solvent. This is best clarified by discussion of the solvent systems shown in Table IV (*15,31-34*).

For the distribution of solutes in the hexane-water system only the v coefficient is large and positive expressing the entropic penalty of cavity formation in water relative to hexane (Table IV). Almost all the other terms apart from r are strongly negative, demonstrating that all these properties (H-bonding, etc.) are more favorable in the aqueous phase. Otherwise, only r, relating to π- and non-bonding interactions, is positive and even its magnitude is small. To illustrate the information made available by this analysis; the striking feature of the 1-octanol-water system is that its basicity is the same as that of water (the a coefficient is zero), whereas its acidity is much less than water as the b term is strongly negative.

Table IV. Abraham Solvent Descriptors for Various Partitioning Systems

Solvent	*c*	*r*(R_2)	*s*(π_2^H)	*a*($\Sigma\alpha_2^H$)	*b*($\Sigma\beta_2^H$)	*v*(V_x)
[C_4mim][PF_6]	-0.16	0.63	-0.004	-1.82	-1.63	2.14
[C_6mim][PF_6]	-0.08	0.14	0.27	-1.48	-2.15	2.31
Hexane	0.36	0.58	-1.72	-3.60	-4.76	4.34
1-Octanol	0.09	0.56	-1.05	0.03	-3.46	3.81
Chloroform	0.13	0.12	-0.37	-3.39	-3.47	4.52
n-Butyl ether	0.18	0.82	-1.50	-0.83	-5.09	4.69

Table IV also illustrates the fact that almost all organic solvent-water systems are characterized by strongly positive v coefficients encapsulating the relative entropic penalty to cavity formation in aqueous phases. However, for the 1-octanol-water system the v coefficient is quite low, ostensibly because of the relatively high equilibrium water content, although one might also point to the increasing degree of structuredness that this may impart to the 1-octanol phase (*35*).

For the ILs it is noticeable that the v coefficient is very small reflecting either a high degree of structuredness or the high equilibrium water content of the phase. Despite this low value, the volume coefficient is still (in common with

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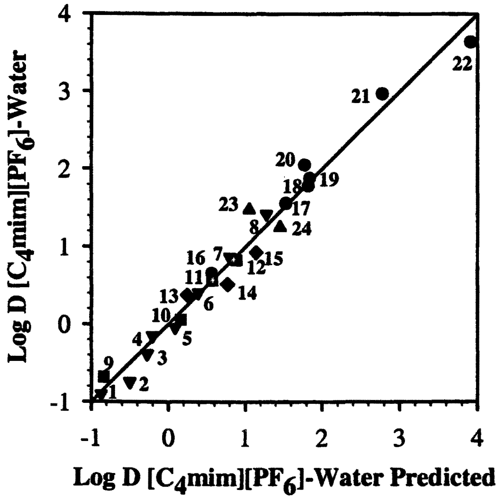

Figure 7. The log of the distribution ratios (D) for a series of small organic molecules (see Figure 5 for solute key) in [C_4mim][PF_6]-water biphasic systems vs. predicted values.

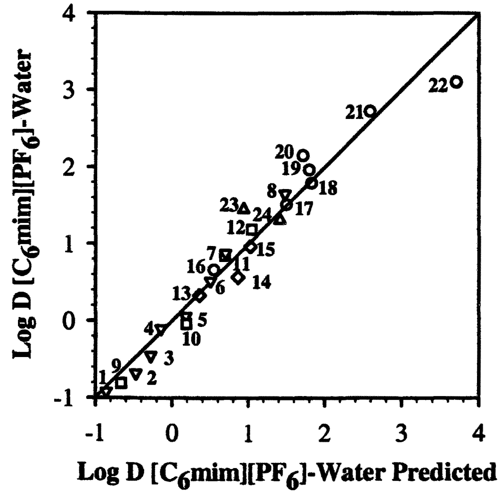

Figure 8. The log of the distribution ratios (D) for a series of small organic molecules (see Figure 5 for key) in [C_6mim][PF_6]-water biphasic systems vs. predicted values.

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Table V. Relative Contribution of Descriptors for $[C_4mim][PF_6]$ and $[C_6mim][PF_6]$-Water Solvent Systems

Coefficients	*Adjusted R^2 $[C_4mim][PF_6]$*	*Adjusted R^2 $[C_6mim][PF_6]$*
v	0.56	0.54
a + v	0.89	0.90
a + b + v	0.93	0.95
a + b + v + r	0.94	0.97
a + b + v + r +s	0.94	0.97
F statistic	73.70	147.20

almost all solvent-water systems) the most important parameter, accounting for over 50% of the variability in the regression, as shown in Table V.

The next most important solute parameters are HBA and HBD, respectively. Large HBAs and HBDs tend to favor partitioning to the aqueous phase reflecting a lower acceptor and donor ability of the IL phase relative to water. This, approximately, confirms the impression created by the determination of the Kamlett and Taft α and β parameters reported earlier, since for the $[C_4mim]$- and $[C_6mim][PF_6]$ ILs, these parameters are lower than or about the same magnitude as water. Only solute molar refractivity, relating to π- and non-bonding interactions, contributes further to the LSER. Thus, to summarize, *the LSER implies that solute volume and molar refractivity will tend to favor partition to the ionic liquid phase whereas solute H-bond donor ability and H-bond acceptor ability will tend to favor distribution to the aqueous phase.*

Conclusions

Our solvatochromatic and partitioning studies of a series of 1-alkyl-3-methylimidazolium ILs, suggest that these solvents are distinguished by relatively high polarity (i.e., of similar magnitude to solvents such as water and *N*-Me-acetamide), but having variable hydrogen bond donating and accepting properties. The comparison of ILs with *N*-Me-acetamide has also just recently been made in the context of lipase catalysis (*36*). The authors draw similar comparisons, but emphasize that at least some ILs do not lead to enzyme inactivation as do molecular solvents of similar polarity.

It appears that the properties of these ILs are strongly influenced by the hydrophobicity and the free energy of hydration of the anion with a change in alkyl chain length having a relatively smaller effect. An example of this is decrease in miscibility of ILs with water as the hydrophobicity of the anion increases from Cl^- to $[BF_4]^-$ to $[PF_6]^-$. It is also worth noting that the ILs studied have overall solvent properties which mark them as being more similar to solvents such as *N*-methyl acetamide and *N*-methyl formamide than to short chain alcohols.

Partitioning data indicates that the presently studied ILs behave in many respects as conventional solvents relative to water, presumably because of the structuredness of the aqueous phase. More detailed studies of the solvent properties of ILs are clearly required in order to fully understand the nature of these interesting solvent systems.

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Chapter 23

Characterization of Hydrophilic and Hydrophobic Ionic Liquids: Alternatives to Volatile Organic Compounds for Liquid–Liquid Separations

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Herein we describe the physical and chemical properties for several Ionic Liquids (ILs) comprised of the 1-alkyl-3-methylimidazolium cation with the Cl^-, Br^-, I^-, BF_4^-, or PF_6^- anions. Liquid-liquid separations with the PF_6^- ILs are highlighted to illustrate their use in "Green Chemistry," as alternatives to traditional organic solvents in separations. The partitioning of organic molecules, combined with IL characterization, has facilitated successful metal ion extraction with both anionic and molecular extractants. This report discusses our current results in the characterization of ILs, their use in liquid-liquid extraction, new concepts for metal ion separations, and solid-state analyses.

Introduction

The curiosity surrounding Ionic Liquids (ILs) has focused on their unique properties, particularly as alternatives to traditional organic solvents in synthesis (*1*) and in liquid-liquid separations from aqueous solutions (*2-6*). Separation processes employing liquid-liquid extractions are a common industrial unit operation, the characteristics of the extracting phase can be fine tuned by selection from the many organic solvents available (*7*). However, most common solvents are volatile organic compounds (VOCs), and their associated chemical behavior (in addition to their potential toxicity) classifies many of them as hazardous substances.

Green Chemistry

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Early social perceptions of chemistry and the chemical industry centered on innovations in medicine, technology, and the overall improvement in the quality of life. More recently, with the rapidly expanding chemical industry, those perceptions have changed and many perceive the industry as a major contributor towards air, land, and water pollution. Each year, the U.S. produces millions of tons of pollution and, at the same time, spends tens of billions of dollars controlling this pollution in the production and cleanup cycle. Therein is the indication that redesigning of chemical production processes may be more effective through targeting source reduction instead of "end of the pipe" waste management or pollution control (*8*). Ideally, pollution would be controlled or minimized at the source, recycling would be done if possible, and any unavoidable waste production would be handled in an appropriate manner.

The chemical industry realizes that their sustained future growth, revenue, and scientific development may depend on considering how their production practices and technologies impact the health and safety of their employees and the environment. Major laws, such as the Clean Air Act and Pollution Prevention Act, have been the impetus for many of these changes (*8*).

Subsequently, the idea of "Green Chemistry" was established to promote the research, development, and implementation of innovative chemical technologies to achieve pollution prevention in a technologically and economically sound manner (*8*). All this would be achieved, from the green chemistry standpoint, through technologies that reduce the consumption or production of hazardous chemicals during the manufacturing or processing of chemical products. A decrease in the generation of hazardous chemicals, along with a diminished potential for health and environmental problems, would be the direct result of a new paradigm for chemical manufacturing or processing.

New Solvent Technologies

Many chemicals that are routinely used are a necessary part of the manufacturing process and yet dangerous to health and the environment. The penchant for traditional solvent extraction systems has come to a crossroads as the emphasis for sustainable technology and green chemistry considers the overall environmental impact of both the process and waste streams generated as a result.

We have been investigating ILs and polymer-based Aqueous Biphasic Systems (ABS) as alternatives to traditional organic solvents in liquid-liquid separations. Although both areas have their own specialized literature, several reports highlight separations based on ILs (*3,10-12*) or ABS (*13-15*) where the merits of both systems show their potential for implementation into industrial separations systems. Most notable from a "Green" perspective is the fact that both ABS and ILs can be used in place of VOCs in liquid-liquid separations. Other work on novel solvent media has shown how supercritical water (*16,17*), supercritical CO_2 (*9*), solventless phases (*18*), and fluorous phases (*19*) can be used in an effort to broaden the scope of possibilities available for more environmentally responsible processes.

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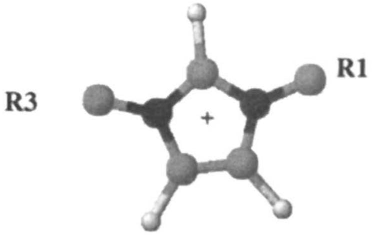
Room Temperature Ionic Liquids (RTILs)

RTILs (or, more generally, ILs), as discussed in this book, are a class of novel compounds composed entirely of ions that, together, melt at or below ambient temperatures (or below 150 °C for ILs) and may be thought to resemble molten ionic melts such as NaCl at 800 °C. While both ILs and molten salts are composed of ions, the presence of organic cations in ILs interrupts the crystal packing and lowers the melting point. Depending on the composition, the resulting IL can be hydrophobic or hydrophilic. An inherent property of many ILs is their miniscule volatility and easily manipulated properties, characteristics of a unique class of solvents. Literature reports are awash with cations for use in these systems, including ammonium (*20-22*), pyridinium (*23,24*), pyrrolidinium (*25*), isoquinolinium (*26*), and imidazolium (*2,27*), each with the possibility for attaching various alkyl groups to the ring or quaternary onium cation. Depending on the type of cation investigated and the length of the alkyl chain, the resulting salts may have a melting point above room temperature and several crystal structures have been reported (*28*).

In our research, we have focused on RTILs incorporating the 1-alkyl-3-methylimidazolium ($[C_nmim]^+$) cation, as shown in Figure 1 (*2-4*). The alkyl group is usually an *n*-alkane and increasing the length of the alkane chain affects the resulting properties (e.g., viscosity, hydrophobicity, and melting point (*2,27*)). For example, $[C_8mim][PF_6]$ is a liquid at room temperature with a glass transition temperature at –75 °C (*2*) and $[C_{10}mim][PF_6]$ melts at 38 °C (*3*). RTILs composed of several different cations or anions (i.e., multi-component mixtures) can be envisaged to further expand the family of ionic liquids.

IL cations and anions can be used to control the water miscibility of the resulting ILs and the choice of anion has been used to the greatest effect on controlling hydrophobicity. 1-alkyl-3-methylimidazolium salts of PF_6^- are water immiscible, BF_4^- salts are water miscible depending on alkyl chain length, and tetrahaloaluminate salts are moisture sensitive. Fluorinated anions such as $N(SO_2CF_3)_2^-$ impart even greater hydrophobicity despite increased expense (*27*).



R3 = CH_3; R1 = *n*-alkane

Figure 1. Generic cations for 1-alkyl-3-methylimidazolium RTILs.

The ionic liquids we have used in our liquid-liquid studies are all liquids below 40 °C, although 150 °C is the adopted upper temperature limit for 'ionic liquid' classification. RTIL is an arbitrary subdivision of ILs that are liquid at room temperature and, thus, facilitate their use at ambient temperatures. Here, we will provide an overview of organic partitioning and metal ion extraction in RTIL-aqueous systems with particular focus on the effects of anion selectivity, increasing alkyl chain length, and cation substitution.

Experimental

The experimental details for the data and procedures reported here are provided in references to physical properties (*2*), organic solute partitioning (*29*), and metal ion extraction (*4-6*). Distribution ratios as reported here are defined as the ratio of the solute concentration in the RTIL lower phase divided by the solute concentration in the aqueous upper phase.

Thymol blue (*3*) partitioning was measured via UV-Vis spectroscopy while the remaining organic solute and metal ion studies reported here utilized radio-labeled chemicals. The methods for chemical and physical characterization of the ILs are described elsewhere (*2*).

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Results

Partitioning of Organic Solutes

Our initial results (*29*) for aromatic solute partitioning between water and $[C_4mim][PF_6]$ indicated that neutral, hydrophobic, aromatic solutes have an affinity for the ionic liquid phase, as shown in Figure 2. For the simple benzene derivatives investigated, partitioning to the RTIL phase generally increased in accordance with the solutes' 1-octanol-water log P values, a common measure of solute hydrophobicity. This demonstrated that partitioning could be achieved and, in many cases, partitioning can be predicted (and/or modeled) using traditional solvent extraction parameters. In this manner, ILs behaved as conventional solvents, displaying a noticeable affinity for aromatic solutes and low aliphatic solubility. Once in the RTIL phase, volatile organic solutes can be removed by distillation or pervaporation, as the RTILs themselves may have negligible vapor pressure. Many non-volatiles can be removed through contact with supercritical CO_2 (*9*). The solubility of $[C_nmim][PF_6]$ in various ethanol-water solutions (*30*) suggests complex solution behavior with increasing mole fractions of traditional solvents.

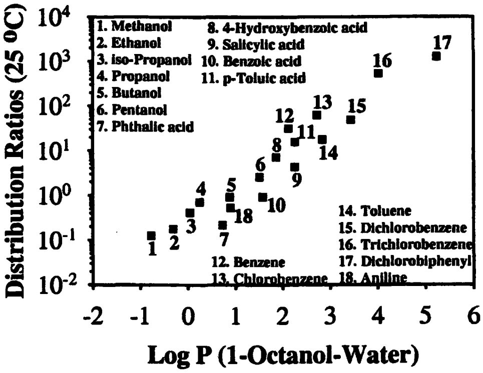

Figure 2. Distribution ratios of organic solutes for the $[C_4mim][PF_6]$-water biphasic system; data from ref. (29).

With charged or ionizable solutes, a change in the aqueous phase pH resulted in certain ionizable solutes exhibiting pH-dependent partitioning such that their affinity for the RTILs decreased upon ionization (*29*). As shown in Figure 3, solute ionization affects the partitioning of aniline and benzoic acid and may be sufficient to cause several orders of magnitude difference in the

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partitioning. Thus, for ionizable solutes, a change in aqueous phase pH could be used for solute recovery from the RTIL phase.

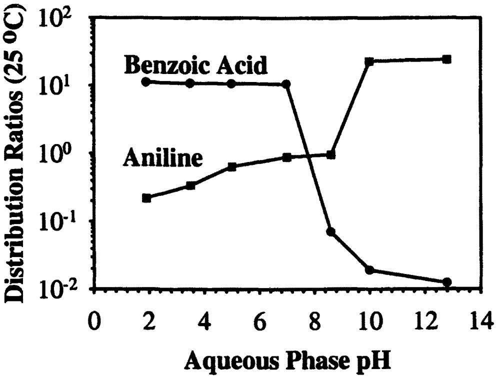

Figure 3. Distribution ratios for aniline (pK_b = 9.42) and benzoic acid (pK_a = 4.19) in [C_4mim][PF_6]-aqueous systems as a function of aqueous phase pH.

Other solutes may have substituent groups that hinder their solubility and partitioning in RTIL-water systems. We have studied the partitioning of unsubstituted, *t*-butyl-, and sulfonated-calixarenes in a series of [$C_n$mim][PF_6]-water systems as a function of aqueous phase pH (*31*). The hydrophobic nature of the RTILs offers an environment suitable for solubilizing the unsubstituted calix-4 and calix-6-arenes, where distribution ratios for both molecules are above 100 and are relatively unaffected by aqueous phase pH. However, the *t*-butyl-calixarenes were not soluble in these RTILs. Adding sulfonate groups to the calixarenes diminished their affinity for the RTIL phase and distribution ratios indicate those molecules prefer the aqueous phase.

We further investigated the pH dependent partitioning of the cationic dye, thymol blue, in these systems (*3*). As depicted in Figure 4, thymol blue preferred the RTIL phase in both the zwitterionic and monoanionic form and partitioned to the aqueous phase under basic conditions. Of the RTILs investigated in liquid-liquid partitioning experiments, thymol blue distribution ratios increased with RTIL hydrophobicity (or lipophilicity) and were highest in [C_8mim][PF_6]. Solid-liquid separations were performed with [C_{10}mim][PF_6] to illustrate how successive heating, mixing, and cooling, combined with appropriate pH changes, could remove thymol blue from an aqueous phase with no retention of the dye upon recrystallization of [C_{10}mim][PF_6] (*3*).

The behavior of organic solutes in RTIL systems illustrates both the unique and unexpected characteristics of RTIL-based separations. With respect to organic solutes, traditional descriptors provide a good indication of solute

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affinity for the RTIL phase. For ionizable molecules, ionization has an apparent effect on phase affinity and may provide a facilitated means for stripping. When selecting or modifying a RTIL, the resulting hydrophobicity has a significant impact on partitioning results.

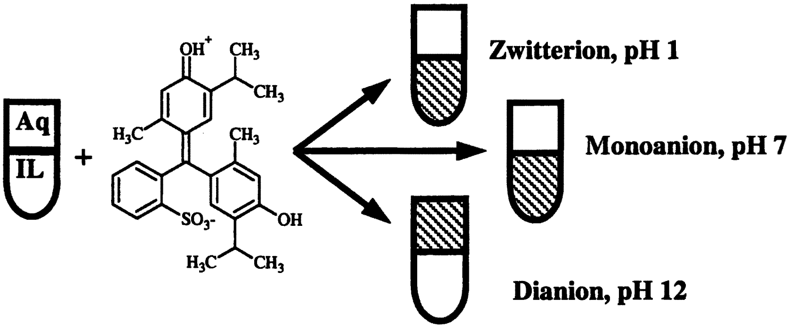

Figure 4. Behavior of thymol blue in [$C_n$mim][PF_6]-aqueous biphasic systems as a function of aqueous phase pH (3).

Metal Ion Extraction

In liquid-liquid separation systems, the hydrated nature of most metal ions lowers their affinity for the extracting phase. This is the case in RTIL systems where hydrated metal ions do not partition to ILs from water (*5,32*). Therefore, it is necessary to change the hydration environment of the metal ion by either using organic ligands (*33-35*) which provide a more hydrophobic region around the metal or form neutral compounds, or with inorganic anions (*36*) that form softer more extractable anionic complexes with the metal. Ideally, in a biphasic system, the extractant would remain in the hydrophobic phase to ensure the complete removal of the metal ions from the aqueous phase. Thus, the challenges in adapting new classes of solvents to traditional separations include finding extractants which quantitatively partition to the solvent phase and can still readily complex target metal ions; or finding conditions under which specific metal ion species can be selectively extracted from aqueous streams containing inorganic complexing ions.

Organic Extractants

Our initial studies used 1-(2-pyridylazo)-napthol (PAN) and 1-(2-thiazolyl)-2-napthol (TAN) as extractants for metal ions in light of their success in

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polymer-based ABS (*37*) and traditional solvent extraction systems (*38*). These are conventional metal extractants widely used in solvent extraction applications. When the aqueous phase is basic, both molecules are ionized, yet they quantitatively partition to [C_6mim][PF_6] over the pH range 1-13. As other reports indicate (*39*), the ionization of the molecules plays an important role in the metal ion extraction, as shown in Figure 5. The distribution ratios for Fe^{3+}, Co^{2+}, and Cd^{2+} show that metal ions could be extracted from the aqueous phase at basic pH and stripped from the RTIL under acidic conditions.

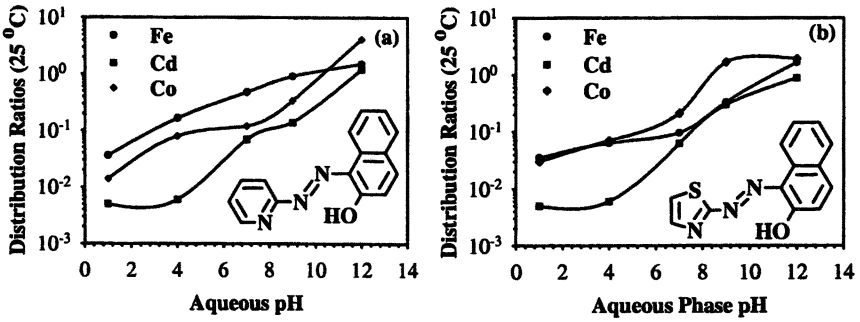

Figure 5. Metal ion distribution ratios with 0.1 mM PAN (a) or TAN (b) in [C_6mim][PF_6]-aqueous systems as a function of aqueous phase pH (37).

Macrocyclic ligands such as crown ethers have been widely used for metal ion extraction (*35,40*). The structure and cavity size of the crown ether is the basis for metal ion selectivity and by attaching alkyl or aromatic ligands to the crown, the hydrophobicity of the ligand can be adjusted. Others have used dicyclohexano-18-crown-6 as an extractant for Sr^{2+} in [$C_n$mim][$N(SO_2CF_3)_2$] RTIL liquid-liquid systems with impressive results (*11*). However, the conditions for optimal extraction in the RTIL system (i.e., low HNO_3 concentrations) were unexpected and contrary to what is typically employed in solvent extraction (*40*). We have used 18-crown-6, dicyclohexano-18-crown-6, and 4,4'-(5')-di-(*t*-butylcyclohexano)-18-crown-6 as extractants for Sr^{2+}, Cs^+, and Na^+ in [$C_n$mim][PF_6]-aqueous systems (*4*). Our results for the partitioning from HNO_3 are contrary to traditional solvent extraction behavior in that while the most hydrophobic extracting phase usually produces the highest distribution ratios, as expected, distribution ratios decrease with increasing acid concentrations.

It was noted, however, that in the presence of increasing HNO_3 (i.e., 1 - 8 M), the degradation of PF_6^- to PO_4^{3-} significantly increased the hydrophilicity of the RTIL phase and produced a monophasic system. Using $Al(NO_3)_3$ as the source of the nitrate anion leads to an increase in distribution ratios (Figure 6) and precluded the degradation of PF_6^- observed at high concentrations of HNO_3. Our results indicate that metal ion partitioning is very complex in RTIL-based liquid-liquid systems and other factors such as aqueous phase composition and water content of the RTILs have dramatic effects on both the metal ion extraction and the stability of the RTILs.

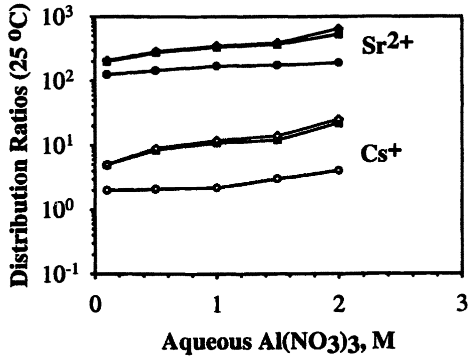

Figure 6. Sr^{2+} and Cs^+ distribution ratios with 0.1 M di-tertbutyl-dicyclohexano-18-crown-6 in $[C_nmim][PF_6]$-aqueous systems ($[C_4mim]^+$ (●), $[C_6mim]^+$ (■), $[C_8mim]^+$ (◆) with increasing aqueous phase concentrations of $Al(NO_3)_3$ (4).

Anionic Extractants

The distribution ratios of certain metal ions may be enhanced in the presence of complexing anions such as halides or pseudohalides. Metal ions such as Hg^{2+} have large formation constants with halides (*41*) and their effect has been observed on the partitioning of Hg^{2+} in other systems (*42*). We have used halides, cyanate, cyanide, and thiocyanate as anionic extractants for metal ion partitioning in $[C_4mim][PF_6]$-aqueous systems (*5*) and the results are shown in Figure 7. For the halides, the formation constants for the series of Hg-I complexes are the highest and decrease to those for Hg-F (*41*). That, in combination with the relative hydrophobicity of the complexes, explains why the iodide complexes produce the highest distribution ratios. The results with the pseudohalides, however, suggest a more complex partitioning mechanism since the Hg-CN complexes have the highest formation constants (*41*), yet display the lowest distribution ratios, similar to data found in other separations systems (*42*).

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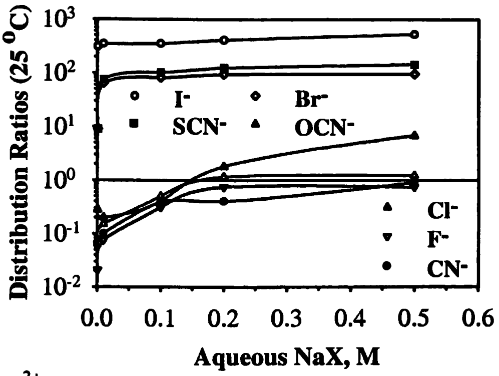

Figure 7. Hg^{2+} distribution ratios with increasing aqueous halide or pseudohalide concentrations in [C_4mim][PF_6]-aqueous systems (5).

Task Specific Ionic Liquids

Through a collaboration with the Davis Group at the University of South Alabama, Task Specific Ionic Liquids (TSILs) have been utilized for metal ion separations. Here, known metal ion ligating groups are incorporated into the cationic moiety of the IL by tethering to the imidazolium cation (Figure 8).

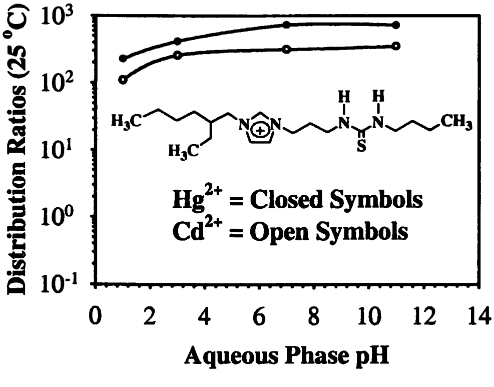

Figure 8. Hg^{2+} and Cd^{2+} distribution ratios from water to RTIL phases comprised of 1:1 combinations of [C_4mim][PF_6] and a TSIL (6).

We have used thioether, urea, and thiourea derivatized imidazolium cations in conjunction with PF_6^- for the extraction of Hg^{2+} and Cd^{2+} (*6*). As shown in Figure 8, distribution ratios are typically higher for Hg^{2+} and a change in the

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aqueous phase pH has a slight effect on the partitioning. (Thus, alternate routes may be necessary for significant metal ion stripping.) Depending on the properties of a specific TSIL, it can be used as the extracting phase or, if the TSIL melts above room temperature, in a combination with [C_4mim][PF_6] as the extracting phase (*6*).

Physical Properties

Utilization of RTILs in solvent extraction technologies requires detailed knowledge of the solvents' physical properties (e.g., hydrophobicity, viscosity, density, surface tension, etc.). Both hydrophobic and hydrophilic RTILs have their niche, although each type may be uniquely suited for certain applications including synthesis, catalysis (*43*), and separations. We have utilized RTILs incorporating either the PF_6^-, $N(SO_2CF_3)_2^-$, and $N(SO_2CF_2CF_3)_2^-$ ([BETI]) anions to produce hydrophobic RTILs suitable for use in place of organic solvents for separations (2). (It should be noted that certain combinations (though not all) of imidazolium and pyridinium cations and $N(SO_2CF_3)_2^-$, $N(SO_2CF_2CF_3)_2^-$, and other hydrophobic anions are covered by U. S. Patent 5,827,602 (*44*).)

Solvent choice can have a substantial effect on the reaction conditions since parameters such as solvent polarity, density, and viscosity impact not only the solute environment, but also the associated engineering considerations. With traditional organic solvents, associated properties include high solute capacity, solute compatibility, and fine-tunability, although it is their volatile nature that has raised the most concern and initiated the search for solvent alternatives.

Table I is a summary of the properties for water-equilibrated [1-alkyl-3-methylimidazolium][PF_6] RTILs, as employed in many of our liquid-liquid experiments. Our previous results (2) indicate water content has a profound effect on certain properties and, in liquid-liquid separation systems analyses after equilibration with water provide the most accurate data needed for engineering RTIL processes under those conditions. The data in Table I is representative for hydrophobic RTILs in comparison to the corresponding hydrophilic RTILs listed in Tables II and III.

Despite the fact that RTILs incorporating the PF_6^- anion sustain biphasic systems, after contact with water they contain a significant, albeit non-stoichiometric, amount of water. We have shown that, for example, the water content for [C_4mim][PF_6] decreases to 590 ppm after a period of drying (*2*), although the resulting [C_4mim][PF_6] is hygroscopic and rapidly adsorbs atmospheric water to return to the saturation point. The RTILs can be successively dried by heating under vacuum. Previous partitioning results show that an increase in the alkyl chain length produces higher distribution ratios (*3*) for hydrophobic solutes, confirming the increase in RTIL hydrophobicity and lipophilicity.

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Table I. Properties of Water-Equilibrated $[C_nmim][PF_6]$ RTILs (2)

Parameter	*$[C_4mim]$ $[PF_6]$*	*$[C_6mim]$ $[PF_6]$*	*$[C_8mim]$ $[PF_6]$*
Water content (ppm)	11700	8837	6666
Viscosity (cP, 25 °C)	397	452	506
Density (g/mL)	1.35	1.24	1.16
Melting point (°C)	4	na[a]	na
Glass transition temperature (°C)	-86	-75	-75
Thermal decomposition (°C, onset)	360	390	374
Surface tension (dyn/cm)	49.8	36.8	34.2

[a] na = transition not observed.

$[C_nmim]^+$ ($n \leq 4$) combined with halides or BF_4^- (*45*) produce hydrophilic ILs that have subtly different properties, as shown in Tables II and III, respectively. In reality, a switch from hydrophilic to hydrophobic RTILs is a continuum that can be modified by changes in anion type and cation substitution. Other cation types, for example PR_4^+, offer alternatives, especially lipophilic, hydrophobic systems which have densities less than 1 which could be used in conventional solvent extraction flotation systems. In Tables II and III, it is important to consider that these RTILs were characterized after being 'dried' for 4 – 5 h at 70 °C under reduced pressure.

Table II. Properties of Dried[a] Hydrophilic $[C_nmim][Cl]$ ILs (2)

Parameter	*$[C_4mim]$ $[Cl]$*	*$[C_6mim]$ $[Cl]$*	*$[C_8mim]$ $[Cl]$*
Water content (ppm)	2200	1130	890
Viscosity (cP, 25 °C)		716	337
Density (g/mL)	1.08	1.03	1.00
Melting point (°C)	41	na	na
Glass transition temperature (°C)	na	-75	-87
Thermal decomposition (°C, onset)	254	253	243
Surface tension (dyn/cm)		42.5	33.8

[a] dried = heating to 70 °C for 4 – 5 h while stirring, under reduced pressure.

The properties in Tables I-III confirm that compromises may be necessary when selecting an optimal IL for a particular application. Although many cation and anion combinations are available, it is evident that concessions must be made between hydrophobicity, viscosity, expense, etc. The majority of these anions are non-coordinating, although the relatively high melting point for

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$[C_4mim][Cl]$ suggests that the cation-anion interactions facilitate hydrogen bonding.

Table III. Properties of Dried[a] Hydrophilic $[C_4mim][BF_4]$ and $[C_4mim][I]$ ILs (2)

Parameter	*$[C_4mim]$ $[BF_4]$*	*$[C_4mim]$ $[I]$*
Water content (ppm)	4530	1870
Viscosity (cP, 25 °C)	219	1110
Density (g/mL)	1.12	1.44
Glass transition temperature (°C)	-97	na
Thermal decomposition (°C, onset)	403	265
Surface tension (dyn/cm)	46.6	54.7

[a] dried = heating to 70 °C for 4 – 5 h while stirring, under reduced pressure.

In general, rheological properties of the RTILs vary with water content. For example, increasing the water content usually reduces viscosity. For $[C_8mim]^+$, the longer alkyl chain produces a more viscous RTIL while $[C_4mim]^+$, by contrast, has the lowest viscosity. Small amounts of chloride remaining from the synthesis may also act to increase the viscosity (*46*).

Density in the ILs described here decreases as the size of the cation increases since the mass of CH_2 is less than that for an imidazolium ring. In addition, as the cation size increases, surface tension decreases which can be attributed to greater charge dispersion over the cation and the associated effect on the cation-anion interactions. Ordinarily, these properties would be expected to change in a similar manner; increasing the cation size would increase both the viscosity and surface tension. Thus, viscosity and surface tension, both parameters that are highly dependent on intermolecular interactions, appear to be determined by different interactions in the ILs.

Thermal properties such as glass transition temperatures and the onset of thermal decomposition are essentially independent of the composition for these $[C_nmim][PF_6]$ RTILs. In general, a class of cations will show glass transition temperatures around a similar temperature range (*25,47,48*). Here, the glass transition temperature is around −80 °C and is close to that for other imidazolium-based RTILs (*45*). A glass transition requires cation and anion reorganization to produce a more ordered material. The addition of CH_2 groups to the alkyl chain may require a minimal amount of additional thermal energy to produce the transition, hence the similarity in these results. Melting points, on the other hand, are not observed for $[C_6mim][PF_6]$ and $[C_8mim][PF_6]$, further supporting the observed tendency for RTILs to supercool.

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When designing a RTIL, fine-tuning the properties can be achieved by changing the cation substituent groups, anion identity, or by mixing two types of RTILs with differing, but defined characteristics. For example, the combination of a TSIL with [C_4mim][PF_6] can be used for Hg^{2+} and Cd^{2+} extraction (*6*). Incorporating anions to produce hydrophilic RTILs illustrates a wider range of properties, as shown in Table II. The effect of anion identity and, as a result, water content on the properties is obvious by comparison of Tables I-III.

Recently, we have prepared a series of RTILs containing 1-alkylisoquinolinium cations, combined with the bis(perfluoroethylsulfonyl)imide ($N(SO_2CF_2CF_3)_2^-$, [BETI]) anion, to produce a new class of ILs. We have also pursued their characterization and use in separations (*26*). The physical properties for [$C_n$isoq][BETI] are summarized in Table IV.

Table IV. Properties of Water-Equilibrated [$C_n$isoq][BETI] ILs (*26*)

n	*Water Content (ppm)*	*Melting Point (°C)*	*Glass Transition (°C)*
4	17700	-62.0	-85.2
6	16200	-77.3	-84.0
8	14900	-68.1	-79.4
10	6900	-59.3	-77.8
12	6600	-51.0	-75.4
14	6100	-49.7	-66.7
16	4700	-48.6	-61.8
18	4100	-47.2	-59.3

As the alkyl chain length ranges from butyl to octadecyl within this series, the hydrophobicity shows an order of magnitude increase. [C_8isoq][BETI] and [C_{14}isoq][BETI] were used in liquid-liquid partitioning experiments for a series of organic molecules (Figure 9) (*26*). Increasing the solute hydrophobicity (as denoted by the 1-octanol-water log P value produces increasing distribution ratios that are slightly higher in [C_{14}isoq][BETI] compared to [C_8isoq][BETI], congruent with the water content. In particular, the distribution ratios for 1,2,4-trichlorobenzene in [C_{14}isoq][BETI] is 1280 (6100 ppm water) compared to 1130 in [C_8isoq][BETI] (14900 ppm water). Using [C_4mim][PF_6] (11700 ppm water) as the extracting phase, the distribution ratio is 524 (*29*).

Here, the composition of the IL makes significant contributions towards the partitioning results. Upon equilibration with water, [C_{14}isoq][BETI] contains more water than water-equilibrated [C_4mim][PF_6] (*2*), although the distribution ratios for 1,2,4-trichlorobenzene are much higher than in [C_4mim][PF_6]. It is not yet clear whether the extended aromatic region in [C_{14}isoq]$^+$ promotes interactions with aromatic solutes or if the observed trends are due to the extended hydrophobic environment offered by the longer alkyl chains.

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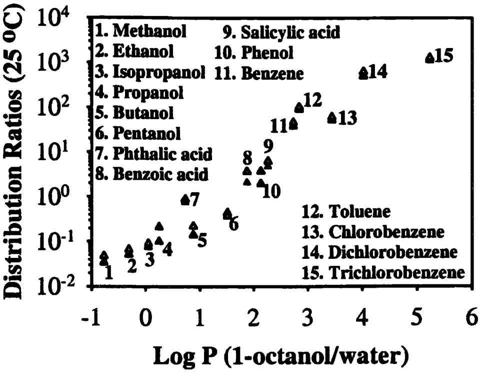

Figure 9. Distribution ratios for organic solutes from water to [C_8isoq][BETI] (▲) or [C_{14}isoq][BETI] (△) systems as a function of the solutes' 1-octanol-water log P values.

Crystal Structures

Since the scientific community has suggested an arbitrary 150 °C as an upper limit on "Ionic Liquid" melting points, there are many cation and anion combinations that produce crystalline materials that can be investigated to further understand the interactions in these systems. Parameters such as cation substitution and anion identity have been selected to investigate their contribution towards the solid state structure of ILs. Initial modeling studies focused on basic [1-methyl-3-ethylimidazolium][$AlCl_4$] systems and two models were proposed for the ionic structures; a stack model in which the anions were located between parallel planes of cations, or one in which Cl^- interacts with each hydrogen on the ring through hydrogen bonding (*49,50*). The crystal structure for [C_2mim][I] shows hydrogen bonding between the anion and the C-2 ring hydrogen (*51*).

For the [$C_n$mim][PF_6] ILs, the length of the alkyl chains and the ring substitution affects the solid state structure of the ILs. The crystal structure for [C_2mim][PF_6] has been reported (*52*) and we have obtained the crystal structure for [C_{10}mim][PF_6] (*32*). [C_{10}mim][PF_6], which melts at 38 °C and has been used in separations at elevated temperatures (*3*), has a unit cell where the cations are oriented in a bilayer arrangement. A similar arrangement has been observed for [C_{12}mim][PF_6] (*24*) where the cation structure also displays a noticeable, and yet unexplained, hook in the alkyl chain.

ILs display essentially 'salt-like' crystal packing in three dimensions for those cations containing short alkyl chains, while a restricted environment about the charged region is present in the bilayer structure for those with longer alkyl chains. The interactions are dominated by ion-ion coulombic interactions in PF_6^-

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structures and change with cation size. Thus, it appears that the key to designing ILs lies in understanding weak interactions that arise in addition to the coulombic interactions. By necessity, the cations and anions will orient themselves in a salt-like manner, but it is the interactions that result from packing frustration that are noticeable in the ILs.

As shown in Figure 10, the cation structures and lattice arrangements show a trend in charged vs. non-charged separations and hydrophobic packing in the structure. The crystal structure for the cation and packing diagram for [1-butyl-2,3-dimethylimidazolium][PF_6] is shown in 10a where no distinct regions of hydrophobicity are observed, owing to the length of the alkyl chain. Adding a methyl group to the C-2 in place of a hydrogen significantly increases the melting point of this IL, considering [C_4mim][PF_6] exists as a glass under practical conditions (2). Figure 10b shows the cation and unit cell for [C_{10}mim][PF_6]. As shown in the packing diagram, the bilayer arrangement dominates the structure, leaving a charge-rich region for the cation ring and anion to interact. Figure 10c shows the cation and lattice arrangement for [C_2mim][PF_6].

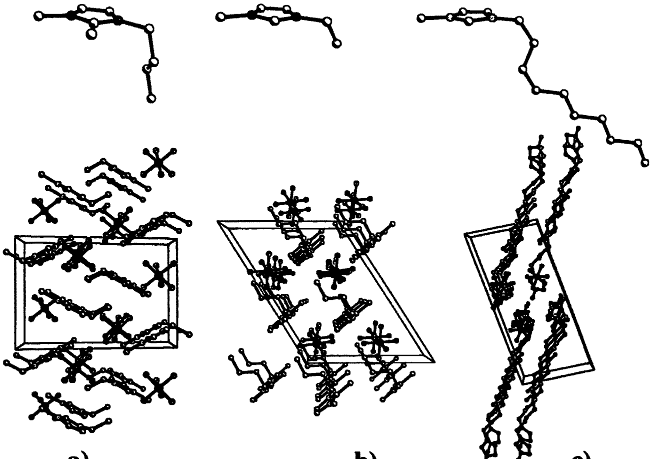

Figure 10. Cation and packing diagrams for three imidazolium-based PF_6^- ILs.

The alkyl chain length appears to have a significant influence on the solid-state structures for imidazolium-based ILs and results in two major types of orientations; salt-like and bilayer. Future solid-state analysis will facilitate the

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understanding of ILs as to what cation and anion structural parameters contribute to stabilizing the resulting IL and the nature of the predominant interactions.

Conclusions

For separations, challenges lie in understanding the partitioning results with regards to those from more traditional systems. Continued study of organic solute behavior in RTIL-based liquid-liquid separations may facilitate a molecular level understanding of the partitioning mechanisms for neutral and ionic solutes, ultimately providing a predictive tool for their behavior. Exploring the driving forces for organic solute partitioning will contribute to the understanding of metal ion extractants, partitioning mechanisms in RTIL systems, and allow incorporation of new concepts such as Task Specific Ionic Liquids for separations.

Beyond the applications of ILs in liquid-liquid systems, the assortment of available and potential hydrophobic and hydrophilic RTILs attests to their easily manipulated physical properties. Through careful selection of cations and anions, significant or subtle changes can be made to the water content and rheological properties of the resulting RTILs. Indeed, crystallographic analyses indicate the structures of ILs result from several types of interactions which depend on the cation substitution and anion type.

The burgeoning field of IL research is producing exciting results and continues to demonstrate the potential for ILs in a variety of applications. Especially from the "Green Chemistry" standpoint, the chemical and physical properties of ILs, combined with their demonstrated utility as solvent replacements, warrants further study and exploration. Thus, the number of new and exciting examples of IL implementation in separations schemes is limited to time and the imagination.

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Chapter 24

Palladium-Catalyzed Carbon–Carbon Coupling Reactions in Room-Temperature Ionic Liquids

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The use of ionic liquids as solvents for carbon-carbon coupling reactions of halogenoarenes is discussed. The generation of palladium imidazolylidene complexes as stable catalytic forms is advanced as the explaination of the observed lack of decomposition.

Introduction

Ionic liquids are attracting a great deal of attention as possible replacements for conventional molecular solvents in a number of synthetic processes.[1] These include reactions of the traditional stoichiometric organic synthesis arsenal and contemporary interests in catalysis for organic synthesis.[2] Features that make ionic liquids attractive include:

- they have no significant vapour pressure, reducing solvent losses and facilitating simple containment;
- they are often composed of poorly coordinating ions, so they have the potential to be highly polar non-coordinating solvents;

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

- they are good solvents for a wide range of both inorganic and organic materials and unusual combinations of reagents can be brought into the same phase;
- they are immiscible with a number of organic solvents and provide a non-aqueous, polar alternative for two-phase systems, hydrophobic ionic liquids can also be used as immiscible polar phases with water.
- they are thermally robust and may be used over a wide range of temperatures.

This has led to their use as solvents for a wide range of processes including: hydrogenation,[3,4] hydroformylation[3] and oligomerisation reactions.[5] Reviews of early applications of ionic liquids to organic synthesis are available.[6] In this paper we will focus on palladium catalysed reactions that lead to the formation of C-C bonds. Among these have been Heck,[7] Suzuki,[8] Stille,[9] and allylic alkylation coupling reactions.[10] Since different workers have used different reactions, direct comparison is difficult. However, it has been shown that reactivity of the haloarenes follows the same trend as seen in molecular solvents with increasing reactivity for heavier halogens.

In conventional molecular solvents these reactions suffer from a number of drawbacks such as catalyst loss into the product, catalyst decomposition and poor reagent solubilities. Many of these problems are greatly reduced or avoided completely when room-temperature ionic liquids are used as the solvents. The question becomes one of whether there is a common reason for the success of these reactions, or is it mearly a coincidence. There are two principal issues of catalyst activity and catalyst stability.

The palladium catalysed coupling reactions have been carried out in phosphonium, ammonium, *N*-alkylated pyridinium and disubstituted imidazolium ionic liquids.[7] We will concentrate on those reactions conducted in disubstituted imidazolium ionic liquids.

The addition of a neutral Group 15 (usually phoshine) donor to the reaction mixture is common to the reactions described.[7-10] The absence of the donor (where it has been reported) leads to minimal reaction and extensive catalyst decomposition to palladium black (e.g. Table I). It is well known that phoshines can act as ligands to stabilize low-valent palladium complexes and as reducing agents to generate palladium(0) species, at least one of which is probably the active catalyst. It has also been shown that the nature of the of the donor has a dramatic effect on both the reactivity and the stability of the system (e.g. Tables II and III). In allylic alkylations electron-donating phoshines (e.g. PCy_3) gave higher rates while more elecron-withdrawing P-donors (e.g. $P(OPh_3)$) gave only low conversions.[10b] The same effect was seen in Heck reactions.[7c] This suggests that the phosphine is directly involved in the catalysis, probably as a ligand in the active catalyst complex.

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Table I. The Heck reaction of iodobenzene and ethyl acrylate to give *trans*-cinnamate in a variety of ionic liquids with 2 mol % $Pd(OAc)_2$.[7c]

Ionic liquid	additive	base	Temp/°C	Time/h	Yield/%
$[C_6py]Cl$	None	Et_3N	40	24	99
$[C_6py]Cl$	None	$NaHCO_3$	40	24	98
$[C_6py][PF_6]$	None	$NaHCO_3$	80	72	42
$[C_6py][BF_4]$	None	$NaHCO_3$	80	72	99
$[bmim][PF_6]$	PPh_3 (4 mol %)	Et_3N	100	1	99
$[C_6py]Cl$	PPh_3 (4 mol %)	$NaHCO_3$	40	24	82
$[C_6py]Cl$	PPh_3 (4 mol %)	$NaHCO_3$	100	24	99
[pmim]Cl	None	Et_3N	80	72	10
[pmim]Cl	None	$NaHCO_3$	100	24	19
$[C_6py]Cl$	DMF	$NaHCO_3$	40	24	77

Table II. The Heck reaction of 4-bromoanisole and ethyl acrylate to give ethyl-4-methoxycinnamate in [bmim][PF_6] with a variety of Group 15 ligands.[7c]

additive	Temp/°C	Time /h	Yield /%
none	100	20	7
PPh_3	100	72	65
$P(tol)_3$	100	24	65
$P(OPh)_3$	100	24	1.5
dppe	100	18	<1
dppf	100	18	<1
$AsPh_3$	100	12	2
$SbPh_3$	100	72	<1

Table III. Allylation of dimethyl malonate in [bmim][PF_6] with a variety of Group phosphine additives.[7c]

Phosphine	Time /h	Conv /%
P^tBu_3	22	75
PCy_3	1	100
P^nBu_3	1	100
$P(4\text{-}C_6H_4OMe)_3$	1	100
PPh_3	6	100
$P(4\text{-}C_6H_4CF_3)_3$	20	0
$P(OPh)_3$	18	0

Results

We have focused on the Suzuki reaction in [bmim][BF_4].[8] The reaction of 4-bromotoluene with phenylboronic acid in [bmim][BF_4] was initially investigated, affording 4-methylbiphenyl in a 69 % yield after 10 min, without catalyst decomposition (Table IV, entry 6). The reaction can also be achieved with one-tenth the catalyst concentration generally required. Once the catalytic solution has been generated the reaction can be conducted under air with similar results and no catalyst decomposition.

The scope of the reaction in [bmim][BF_4] was investigated with electron-rich and electron-deficient halogenoarenes (Table IV). Notably, 4-methoxybiphenyl is afforded in a 40% yield in 6 h (2 TON h^{-1}) applying the original conditions. In [bmim][BF_4] an 81% yield is afforded in 10 min (401 TON h^{-1}, Table IV, entry

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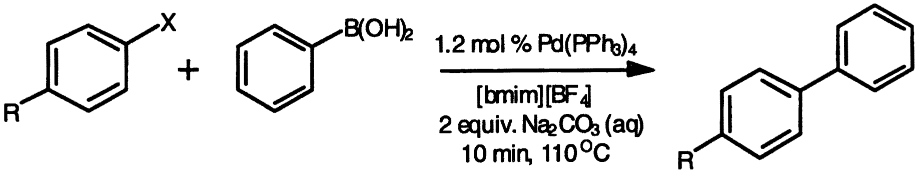
7), which is in the order of 200 times the original reactivity. Despite these enhancements, chlorobenzene was still inactive even after 3 h.[13]

Table IV. Scope of the Suzuki cross-coupling reaction in [bmim][BF_4]: variation of the arylhalide.



Entry	X	R	Yield (%)[a]	TON	TON h^{-1}
1	I	H	86 (95)	72	430
2	Br	H	93 (95)	78	465
3	Cl	H	1 (1)	1	5
4	Br	Cl	17	14	85
5	Br	$COCH_3$	67 (97)	56	335
6	Br	CH_3	69 (92)	58	345
7	Br	OCH_3	81 (92)	67	401

[a] Isolated yields of corresponding cross coupled product based on arylhalide. Purity confirmed by GC, GC-MS and ^1H NMR. Isolated yields after 3 h in parenthesis.

During our investigations of the optimization of the Suzuki reaction in ionic liquids, we noted that the quality of the reactions and the stability of the catalyst in solution was unreliable. Further investigation revealed that this was dependent upon the batch of ionic liquid being used. After initially demonstrating that the addition of a large amount of [bmim]Cl to the reaction mixture hindered the reaction, but did not lead to obvious precipitation of palladium black we realized that the addition of a source of halide ions prevented the decomposition of the palladium catalyst and lead to higher yielding reactions (Table V). It was determined that a ratio of 4 equivalents of halide with respect to the palladium was required to prevent visable evidence of catalyst decomposition. Hence, we chose to investigate this phenomenon.

It is well known that the first step in the catalytic cycle is the oxidative addition of the haloarene (or acetate in allylic alkylations) to a palladium(0) complex. In our investigations of the ^{31}P NMR studies of the addition of bromobenzene to an ionic liquid containing $Pd(PPh_3)_4$ clearly demonstrates the formation of $PhPd(PPh_3)_2Br$ (**1a**, δ = 23.3 ppm). When aqueous Na_2CO_3 is

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added to this solution in the presence of NaCl, a strong signal due to $OPPh_3$ is observed, with two new signals at 22.6 and 21.8 ppm, respectively. Subsequent ESI-MS revealed the presence of $[(PPh_3)_2Pd(bmimy)X]^+$ {where: (bmimy) = 1-butyl-3-methylimidazolylidene, X = Cl (**3a**) or Br (**3b**)}. The assignments of these spectra were achieved by comparison to ionic liquid solutions of independently prepared samples. The analogous $[(PPh_3)_2Pd(pyimypy)Br]Br$ {where: (pyimypy) = 1,3-bis(2-pyridyl) imidazolylidene} complex has recently been prepared by the addition of 1:1 molar ratio of [pyimypyH]Br to $Pd(OAc)_2$ in the presence of PPh_3 and KBr in THF.[11] In addition, the related neutral complex, $[(PR_3)Pd(peimy)I_2]$ {where: (peimy) = 1,3-di(1′-(*R*)-phenylethylimidazolylidene} and PR_3 = PPh_3 and PCy_3} has also been reported.[12] Finally $[(PPh_3)_2Pt(tmimy)I][BF_4]$ {where (tmimy) = 1,3,4,5-tetramethylimidazolylidene} complex has recently been described.[13]

Table V. The effect of added [bmim]Cl on the Suzuki reaction of 4-bromotoluene and phenylboronic acid

	Yield / %	TON h^{-1}
$[bmim][BF_4]$	30	150
$[bmim][BF_4]$ + [bmim]Cl (4:1 c.f. Pd)	66	330
$[bmim][BF_4]$ + [bmim]Cl (1:1 c.f. 4-bromotoluene)	12.9	1.33

In the absence of an aryl bromide under otherwise similar conditions, **3a** was detected only in trace amounts. Complex **3** was also detected using **2** as the source of palladium, either added directly or prepared *in-situ* from $Pd(OAc)_2$, or $PdCl_2$, both with additional PPh_3. Employing these sources of palladium in the absence of the aryl bromide afforded only **3a**. Hence, the formation of **3b** in the ionic liquid is the result of the presence of bromide ions originating from the oxidative addition product.

In a few cases where **3a** was detected from $Pd(PPh_3)_4$ without the addition of NaCl, subsequent analysis of the ionic liquid showed that residual chloride from its preparation, by metathesis of [bmim]Cl with $Na[BF_4]$, was still present. After additional washing of the ionic liquid, reactions in these batches of $[bmim][BF_4]$ failed to afford **3a** without a chloride additive.

One final source of **3** was identified. When independently prepared samples of **1**[14] were used as the palladium source and the reaction mixture was slowly heated, **3** was also detected, without the need to add NaCl. This indicates that the oxidative addition product **1** is capable of acting as the source of halide.

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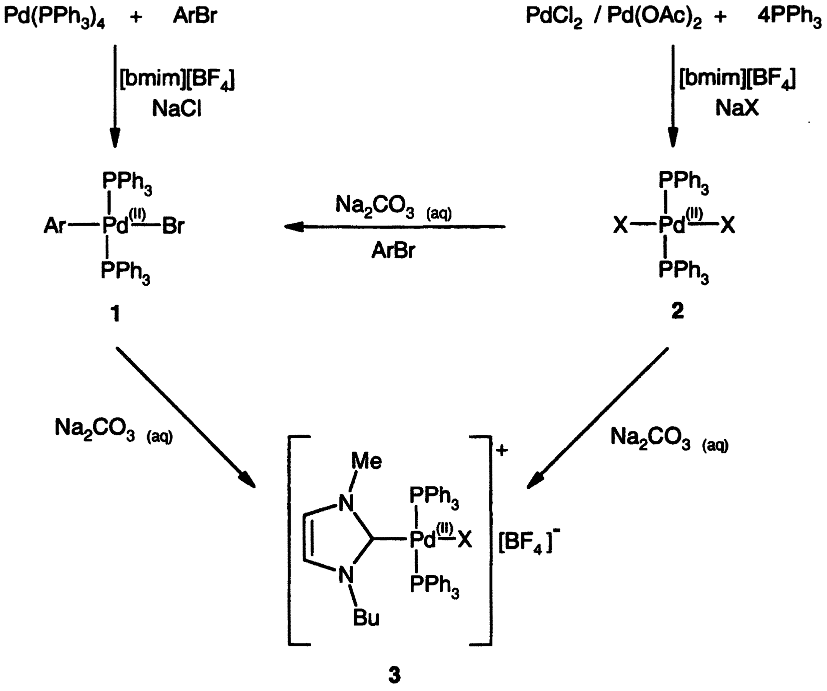
Scheme


Pd(PPh3)4 + ArBr
[bmim][BF4]
NaCl
PdCl2 / Pd(OAc)2 + 4PPh3
[bmim][BF4]
NaX
PPh3
Ar—Pd(II)—Br
PPh3
1
Na2CO3 (aq)
ArBr
PPh3
X—Pd(II)—X
PPh3
2
Na2CO3 (aq)
Na2CO3 (aq)
Me
N
N
Bu
PPh3
Pd(II)—X
PPh3
+
[BF4]-
3

	X	Ar	^{31}P NMR	ESI$^+$ MS
1a	-	Ph	24.2	707 $[PhPd(PPh_3)_2]^+$
1b	-	py	24.6	788 $[HpyPd(PPh_3)_2Br]^+$
2a	Cl	-	23.9	665 $[Pd(PPh_3)_2Cl]^+$
2b	Br	-	22.6	709 $[Pd(PPh_3)_2Br]^+$
3a	Cl	-	20.7	803 $[(PPh_3)_2Pd(bmimy)Cl]^+$
3b	Br	-	19.6	849 $[(PPh_3)_2Pd(bmimy)Br]^+$

A single crystal X-ray study of **3a** shows the complex to have crystallographic C_s symmetry about a plane that includes the palladium and chlorine atoms and the imidazolylidene ring system; the *n*-butyl chain is disordered above and below the

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mirror plane (Figure 1).[1] The imidazolylidene ring is oriented orthogonally to the palladium coordination plane. The geometry at palladium is only very slightly distorted square plane with *cis*-angles ranging between 89.54(7) and 90.54(6)°. The palladium coordination distances are unexceptional. The palladium and its four coordinated atoms are planar to only 0.12 Å, the deviation being a consequence of a distinct non-linearity in the C–Pd–Cl angle [171.1(4)°]; the P–Pd–P angle is essentially linear [178.58(12)°]. There are no intermolecular contacts of note.

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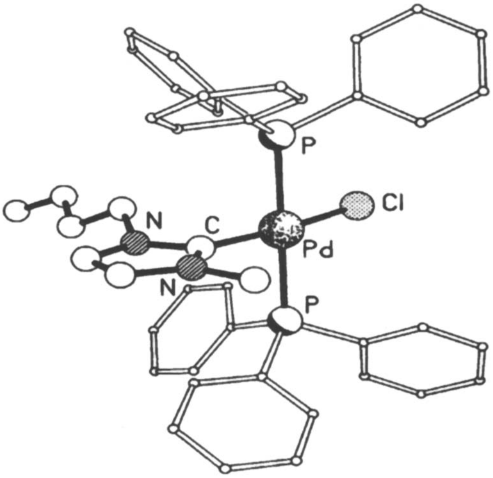

Figure 1. The molecular structure of **3a**. Selected bond lengths (Å), Pd–P2.350(2), Pd–Cl 2.333(4), Pd–C 1.999(13).

The use of transition metal imidazolylidene complexes as catalysts has attracted much attention, particularly in palladium catalysed coupling reactions.[15] There has been some speculation that the formation of palladium imidazolylidene complexes may explain the success of many of these reactions.[7c] Hence, the *in situ* formation of **3** from [bmim][BF_4] has implications for a number of palladium-phosphine catalysed coupling reactions in disubstituted imidazolium based ionic liquids. While some reports suggest that the observed enhancements in such reactions can be explained in terms of the unique ionic liquid environment, the involvement of these complexes prepared *in-situ* cannot be discounted. This is especially true when adventitious Cl^- may be present. Our preliminary results demonstrate that **3** is extremely active in the Suzuki cross coupling reaction. Notably, bromobenzene couples with phenylboronic acid affording biphenyl in a 95 % yield (930 TON h^{-1}) without any noticeable catalyst decomposition. Repetitive catalytic runs are also possible without any appreciable lose in activity.

---

[1] *Crystal data for* **3a**: $[C_{44}H_{44}N_2P_2ClPd][BF_4] \cdot 2CHCl_3$, $M = 1130.2$, orthorhombic, space group *Pnma* (no. 62), $a = 18.193(4)$, $b = 23.392(2)$, $c = 11.883(3)$ Å, $V = 5057(2)$ Å^3, $Z = 4$ (C_s symmetry), $D_c = 1.484$ g cm^{-3}, •(Cu-K•) = 7.37 mm^{-1}, $T = 293$ K, colourless platy needles; 3570 independent measured reflections, F^2 refinement, $R_1 = 0.081$, $wR_2 = 0.211$, 2313 independent observed absorption corrected reflections [$|F_o| > 4$•($|F_o|$), 2• • 120°], 298 parameters. The high value for R_1 is a consequence of disorder in the BF_4 counterion and the chloroform solvent molecules.

Finally we investigated the conditions under which bis(imidazolylidene)palladium dihalide complexes are formed in [bmim][BF_4]. Firm evidence for the *in situ* formation of bis(imidazolylidene)palladium dibromide in 1-butyl-3-methylimidazolium bromide {[bmim]Br} was first reported by J. Xiao *et. al.*.[7e] In agreement with these results,[7e] using $Pd(OAc)_2$ as the palladium souce in [bmim][BF_4] without the addition of phosphine or a halide source fails to generate any imidazolylidene complexes. Addition of 4 equivolents (*cf.* palladium) of NaBr, leads to the formation of $(bmimy)_2PdBr_2$. However, addition of NaCl fails to produce$(bmimy)_2PdCl_2$. We are continuing to investigate this result.

In summary, we have detected the *in situ* formation of the mixed phosphine imidazolylidene palladium complex, **3**, from [bmim][BF_4] under conditions similar to many ionic liquid mediated palladium catalysed coupling reactions. Further, we have demonstrated that a range of palladium sources can be employed. We are continuing to investigate the scope of the catalytic activity of **3** and analogous complexes in a wide range of palladium-catalysed reactions.

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Experimental Section

$[(PPh_3)_2Pd(bmimy)Cl]$ $[BF_4]$ (3a). To a mixture of $(PPh_3)_2PdCl_2$ (1.38 g, 1.96 mmol), NaCl (1.14 g, 19.6 mmol), [bmim][BF_4] (384 mg, 1.70 mmol) and PPh_3 (1.03 g, 3.93 mmol) in de-oxygenated THF (75 cm^3) was injected a solution Na_2CO_3 (3.60 g, 34.0 mmol) in H_2O (10 cm^3) under N_2. The bright yellow mixture was heated to reflux for 7 h , cooled to room temperature then cannular filtered keeping the filtrate under N_2. Diethyl ether (100 cm^3) was then added to the filtrate and kept at 0 °C for 2.5 h, then cannular filtered. The yellow solid was re-crystallization from chloroform/hexane to afford **1** as a white crystalline solid (0.99 g, 56.4 %). ^1H NMR ($CDCl_3$) 0.69 (t, *J* = 7 Hz, 3H, $N(CH_2)_3C\mathit{H}_3$), 1.06 (m, 4H, $NCH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 3.02 (s, 3H, $NC\mathit{H}_3$), 3.51 (m, 2H, $NC\mathit{H}_2(CH_2)_2CH_3$), 6.81 (m, 1H, $NC\mathit{H}$), 6.93 (m, 1H, $NC\mathit{H}$), 7.39–7.54 (m, 30H, $(P(C_6H_5)_3)_2$); ^{13}C NMR ($CDCl_3$) 13.2 (s, 1C, $N(CH_2)_3\mathit{C}H_3$), 19.9 (s, 1C, $N(CH_2)_2\mathit{C}H_2CH_3$)), 31.1 (s, 1C, $NCH_2\mathit{C}H_2CH_2CH_3$), 36.9 (s, 1C, $N\mathit{C}H$-

$_2$(CH$_2$)$_2$CH$_3$), 50.6 (s, 1C, NCH$_3$), 123.3 (s, 1C, NCH), 126.3 (s, 1C, NCH), 128.3 (t, *J* = 25.3 Hz, 6C, P(1-C_6H$_5$)$_6$), 129.1 (t, *J* = 5.4 Hz , 12C, P(2-C_6H$_5$)$_3$), 131.7 (s, 6C, P(4-C_6H$_5$)$_3$), 133.8 (t, *J* = 6.1 Hz, 12C, P(3-C_6H$_5$)$_3$), 158.7 (s, 1C, N$_2\mathit{C}$); ^{31}P NMR (CDCl$_3$) 20.7 (2P, s, PPh$_3$); IR (KBr) 3054, 2932, 1572, 1482, 1435, 1096, 1057, 999, 747, 695, 523, 496; ESI$^+$-MS (m/z) 803 ([(PPh$_3$)$_2$Pd(bmiy)Cl]$^+$, 100 %), 541 ([PPh$_3$Pd(bmiy)Cl]$^+$, 35 %); ESI$^-$-MS (m/z) 87 ([BF$_4$]$^-$, 100 %); mp 196–199 °C.

[(PPh$_3$)$_2$Pd(bmiy)Br][BF$_4$] (3b). As for **3a** except NaBr (2.02 g, 19.6 mmol) added to afford **2** as an off-white crystalline solid (1.63 g, 88.7 %). ^{1}H NMR (CDCl$_3$) 0.71 (t, *J* = 7 Hz, 3H, N(CH$_2$)$_3$CH_3), 1.10 (m, 4H, NCH$_2$CH_2CH_2CH$_3$), 3.01 (s, 3H, NCH_3), 3.57 (m, 2H, NCH_2(CH$_2$)$_2$CH$_3$), 6.80 (m, 1H, NCH), 6.84 (m, 1H, NCH), 7.41–7.52 (m, 30H, (P(C$_6$H$_5$)$_3$)$_2$); ^{13}C NMR (CDCl$_3$) 13.3 (s, 1C, N(CH$_2$)$_3\mathit{C}$H$_3$), 20.0 (s, 1C, N(CH$_2$)$_2\mathit{C}$H$_2$CH$_3$)), 31.0 (s, 1C, NCH$_2\mathit{C}$H$_2$CH$_2$CH$_3$), 36.8 (s, 1C, NCH$_2$(CH$_2$)$_2$CH$_3$), 50.6 (s, 1C, NCH$_3$), 123.2 (s, 1C, NCH), 126.2 (s, 1C, NCH), 128.9 (t, *J* = 25.4 Hz, 6C, P(1-C_6H$_5$)$_3$) 129.0 (t, *J* = 5.4 Hz, 12C, P(2-C_6H$_5$)$_3$, 131.6 (s, 6C, P(4-C_6H$_5$)$_3$), 133.9 (t, *J* = 6.1 Hz, 12C, P(3-C_6H$_5$)$_3$, 158.7 (s, 1C, N$_2\mathit{C}$); ^{31}P NMR (CDCl$_3$) 19.6 (2P, s, PPh$_3$); IR (KBr) 3058, 2929, 1552, 1487, 1432, 1097, 1082, 983, 728, 585, 561, 443; ESI$^+$-MS (m/z) 849 ([(PPh$_3$)$_2$Pd(bmiy)Br]$^+$, 100 %), 587 ([PPh$_3$Pd(bmiy)Br]$^+$, 35 %); ESI$^-$-MS (m/z) 87 ([BF$_4$]$^-$, 100 %); mp 172–173 °C.

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Chapter 25

Catalytic Oxidations in Ionic Liquids

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Catalytic epoxidations have recently been shown to proceed with high yield and high selectivity using ambient temperature ionic liquids based on the *N*, *N'*-dialkylimidazolium cation. Jacobsen's chiral (salen)Mn^{III} epoxidation catalyst gives the epoxide of 2,2-dimethylchromene in 96% enantiomeric excess and recycles easily when used with the ionic liquid [bmim]PF_6. Methyltrioxorhenium reacts with hydrogen peroxide in [emim]BF_4 to catalyze olefin epoxidation with yields > 99%. These two systems serve as glimpses of the possibilities for "green" oxidations using ionic liquids.

Introduction

Oxygen atom transfer is one of the most fundamentally important chemical reactions. Incredible volumes of industrial chemicals are made directly from the catalytic oxidations of hydrocarbons (*1*). Catalytic oxidations are also extremely important reactions in the synthesis of fine chemicals, especially pharmaceuticals. Nevertheless, industrial oxidations are some of the most environmentally noxious reactions, employing such toxic reagents as permanganates, osmium tetraoxide, chromates, and *meta*-chloroperoxybenzoic acid (*m*-CPBA). These reagents also yield quite large amounts of salt byproducts; the waste:product ratios for the production of pharmaceuticals generally ranges around 25-100 kg byproducts:1 kg products (*1*). Additionally, these harsh reagents are used in volatile organic reaction media, compounding the environmental and economic problems of waste management and disposal from fundamental oxygen-transfer reactions.

The development of "green" chemical transformations is an increasingly important area of concern (*2*). Both industry and academia are heavily involved in the development of catalytic processes that use environmentally benign oxidants. The best oxidant of all, with respect to byproduct formation, is molecular oxygen, but its use as an effective oxidant is largely limited to the production of industrial chemicals (*1*). Molecular oxygen is most often not a viable economic option for catalytic oxidations to synthesize fine chemicals (*1*).

An excellent second choice is hydrogen peroxide, which can transfer an oxygen atom and yield only water as the byproduct. Stoichiometric oxidations with hydrogen peroxide either are too slow to be realistic or suffer from low selectivities because of product formation through radical pathways (*3*). However, a number of high-valent transition metal complexes [and low valent complexes in the case of Pd(II) and Pt(II)] are capable of activating hydrogen peroxide for oxygen transfer (*4*) to a wide variety of substrates. Additionally, metal-catalyzed activation of hydrogen peroxide can be applied to both heterogeneous and homogeneous catalytic processes, making hydrogen peroxide a widely applicable "green oxidant."

Epoxides are an important class of compounds because of their high value as starting materials for organic synthesis (*5*). Industrially, the best-known example of olefin epoxidation using peroxides is the production of propylene oxide from alkyl hydroperoxides catalyzed by high-valent early transition metal complexes (*1*). Otherwise, epoxidation is accomplished industrially using peracids, especially *m*-CPBA, performic acid, and peracetic acid (*5*).

Much attention has been given to ionic liquids in recent years towards the pursuit of cleaner chemistry (*6*, *7*). The air- and water-stable ionic liquids, particularly the dialkylimidazolium salts, seem to be particularly well suited for oxidations (*7*). The combination of the nonvolatility and recyclability of ionic liquids with transition-metal-catalyzed oxidations employing benign oxidants offers great promise towards effecting clean oxidations. To date, only two reports of successful oxygen-atom transfer reactions using ionic liquids have surfaced; hence, this account will cover both systems in detail.

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The (Salen)Mn^{III} Epoxidation System

The first use of ionic liquids in catalytic oxidations was reported in 2000 by Song and Roh (*8*). Jacobsen's chiral (salen)Mn catalyst (*9*, *10*), Figure 1, was used to epoxidize a series of olefins with high enantioselectivity.

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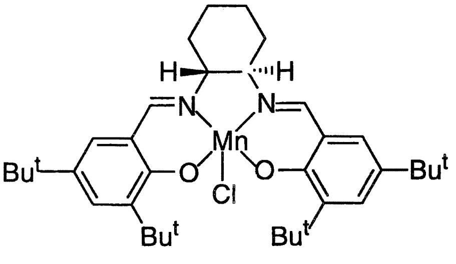


Figure 1. Jacobsen's chiral (salen)Mn^{III} catalyst.

As Song and Roh point out, there have been numerous attempts to immobilize this complex, but none have been successful (*11-15*). However, using the hydrophobic ionic liquid *N*-butyl-*N'*-methylimidazolium hexafluorophosphate ([bmim]PF_6) creates an efficient heterogeneous system when aqueous sodium hypochlorite is employed as the oxidant. A 1:4 (v/v) mixture of [bmim]PF_6:CH_2Cl_2 dissolves the catalyst and forms the more dense phase, and the olefin added to an aqueous, buffered solution of hypochlorite constitutes the less dense phase. The net reaction is shown in Figure 2 for the oxidation of 2,2-dimethylchromene.

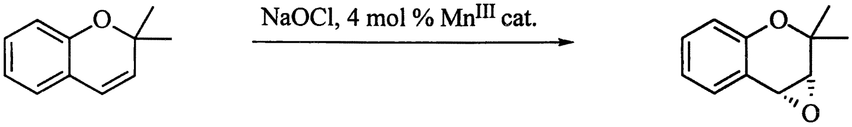
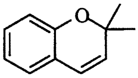
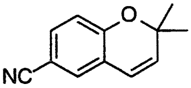
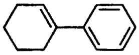
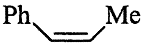
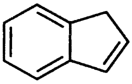


Figure 2. Epoxidation of 2,2-dimethylchromene.

The above reaction has been used for several different olefins. The olefin yields and enantioselectivities are shown in Table 1. There are numerous advantages to this system. As evident from Table 1, the epoxide yields and enantioselectivities are rather favorable. The system employs a transition metal catalyst instead of a stoichiometric amount of a harsher oxidizer (*vide supra*). Perhaps the greatest advantage, though, is gained through the use of the ionic liquid. The products and leftover reactants stay in the organic phase of the reaction and are removed from the catalyst solution by distillation. Purification on a column of silica gel with 1:10 ethyl acetate:hexane yields the pure epoxide product. The catalyst solution is then reused as is without purification. Unfortunately, this system does suffer from catalyst decomposition with each use. While the epoxidation of 2,2-dimethylchromene gives an 86% epoxide yield in 96% ee during the first use, the yield goes down to 53% by the fifth use with slightly decreased ee (88%).

Table 1. Asymmetric Epoxidation with Mn^{III}/ClO^- using $[bmim]PF_6$

Substrate	*Time (h)*	*Yield (%)*	*ee (%)*
	2	86	96
	4	72	94
	4	77	84
	3	72	86
	4	72	84

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Reaction Acceleration and Catalyst Decompostion

It is also reported that the epoxidation of 2,2-dimethylchromene proceeds faster when $[bmim]PF_6$ is added to the organic phase. In the control experiment without $[bmim]PF_6$, the reaction requires 6 hours to reach the same conversion that is achieved in only 2 hours when 1:4 $[bmim]PF_6$:CH_2Cl_2 is used. Reaction acceleration when ionic liquids are used in a biphasic system is precedented (*16, 17*).

Both the reaction acceleration and the catalyst decomposition may very well be attributable to the ionic liquid. It has recently been reported that water is soluble in the hydrophobic ionic liquid $[bmim]PF_6$ up to approximately 1.735 M (*18*). This limited miscibility could be responsible for accelerating the reaction by introducing small amounts of the catalyst homogeneously into the aqueous phase. Conversely, this introduction of small amounts of the catalyst into the aqueous phase may be leading to slow decomposition of the catalyst.

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MTO-Catalyzed Epoxidations Using Hydrogen Peroxide

Since the 1991 discovery of its catalytic activity, methyltrioxorhenium (MTO) has proven to be an exceptionally versatile oxidation catalyst (*19*, *20*). The catalyst is air- and water-stable and soluble in a wide range of solvents. Initially shown to be an efficient olefin oxidizer, MTO's catalytic ability has been extended to oxidizing amines, sulfides, hydrocarbons, silanes, and aromatics using hydrogen peroxide as the stoichiometric oxidant (*21-23*). MTO reacts with one and two equivalents of hydrogen peroxide to form a monoperoxorhenium complex (**A**) and a diperoxorhenium complex (**B**), respectively. The peroxorhenium complexes transfer an oxygen atom to a reactive substrate, and the reactions yield water as the byproduct, Figure 3.

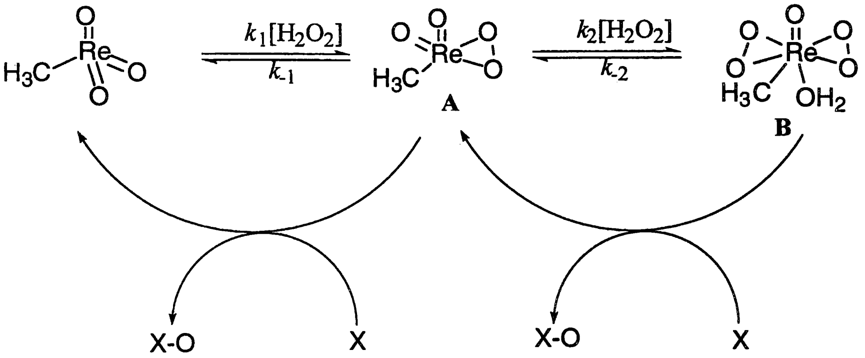

Figure 3. Formation and reactivity of active catalytic species in the MTO system.

The advantages of the MTO/H_2O_2 oxidation system are numerous. Olefin epoxidation, for example, proceeds with yields typically exceeding 95%, and the oxidations can be performed at low concentrations of peroxide and at room temperature. Most importantly, the MTO/H_2O_2 system affords high yields while producing water as the sole byproduct.

One of the few drawbacks of the MTO/H_2O_2 system for olefin epoxidation is that the use of aqueous hydrogen peroxide can lead to ring-opening of the epoxide products. This problem can be circumvented by a few different methods, the most important of which is the use of a water-free peroxide source. Bis(trimethylsilyl)peroxide (*24*, *25*) and urea hydrogen peroxide (UHP) (*26*) have been shown to be effective oxidants while yielding the epoxide product almost exclusively over the diol.

Recently, the advantages of ionic liquids and the MTO/peroxide system have been combined to create an oxidation solution that is both environmentally

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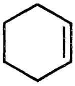
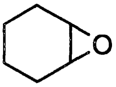
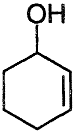
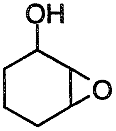
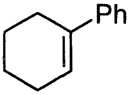
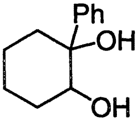
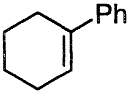
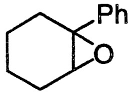
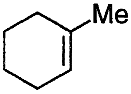
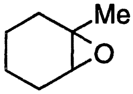
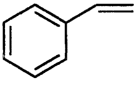
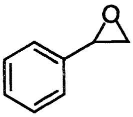
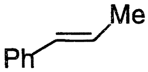
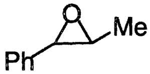
friendly and highly efficient. The ionic liquid *N*-ethyl-*N*'-methylimidazolium tetrafluoroborate ([emim]BF_4) is used with MTO and urea hydrogen peroxide to oxidize a series of olefins and allylic alcohols with high conversion and high epoxide yield (*27*). This system offers the advantages of heterogeneous catalysis in a homogeneous solution: the products are easily removed by simple extraction with diethyl ether, and the reaction times are comparable to those using organic molecular solvents. A summary of the epoxide yields is provided in Table 2.

Table 2. Epoxidation of Olefins and Allylic Alcohols with MTO/UHP in [emim]BF_4.[a]

Entry	*Substrate*	*Oxidant*	*Product*	*Yield (%)*[b]
1		UHP		≥ 99
2		UHP		94[c]
3		30% H_2O_2		≥ 95
4		UHP		≥ 95
5		UHP		≥ 95
6		UHP		≥ 95
7		UHP		≥ 95

[a] Conditions: 0.5 M substrate, 1.0 M oxidant, 2 mol % MTO, 2.0 mL [emim]BF_4, room temperature, 8 h.

[b] Yields determined by ^1H NMR and GC-MS.

[c] Major products are 2,3-epoxycyclohexanol (62%) and 2,3-epoxycyclohexanone (32%).

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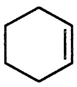
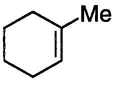
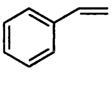
Excellent results are obtained with this unique oxidation solution. The importance of water-free conditions for the recovery of epoxides sensitive to ring-opening is illustrated in entries 3 and 4. The 1,2-diol is the major product when aqueous hydrogen peroxide is used, but using UHP yields the epoxide almost exclusively. It should be noted that the ionic liquid must be dried under vacuum in order to remove traces of water before the reagents were added.

One of the primary differences in the MTO/UHP chemistry in ionic liquids compared to that in molecular solvents is the solubility of urea hydrogen peroxide. The UHP adduct is sparingly soluble in molecular solvents (H_2O, $CHCl_3$, CH_2Cl_2), but UHP is readily soluble in [emim]BF_4. This difference in solubility may account for the differences in reaction times between the two oxidation solutions. As shown in Table 3, the epoxidation of styrene in particular proceeds much faster in [emim]BF_4 than in $CDCl_3$.

Table 3. Olefin Epoxidation in Molecular and Ionic Solvents.[a]

Entry	*Substrate*	*Solvent*	*Time (h)*	*Conv. (%)*	*Epoxide yield (%)*
1		$CDCl_3$	18	98	99
		[emim]BF_4	≤ 8	≥ 95	99
2		$CDCl_3$	19	88	96
		[emim]BF_4	≤ 8	≥ 95	≥ 95
3		$CDCl_3$	19	46	≥ 95
		[emim]BF_4	≤ 8	95	≥ 95

[a]Olefin:oxidant:MTO = 1:1:0.01 in $CDCl_3$ reactions (*26*), 1:2:0.02 in [emim]BF_4 reactions (*27*).

The major advantage of MTO, besides its efficient catalytic ability, is the fact that it uses hydrogen peroxide as the stoichiometric oxidant, creating water as the sole byproduct. In this regard, the MTO/H_2O_2 system is much more favorable than the (salen)Mn^{III} catalysts (*vide supra*), as the manganese catalysts employ aqueous hypochlorite. Hypochlorite solutions are not nearly so environmentally friendly as aqueous hydrogen peroxide, and the byproduct of the Mn^{III}/ClO^- catalytic cycle is Cl^-, which has to be removed from the products.

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Limitations of the MTO/Peroxide System in Ionic Liquids

The MTO/peroxide oxidation cycle is sensitive to bases and halides, so solvent purity is of the utmost importance for succesful epoxidations. The base-catalyzed decompostion of MTO has been thoroughly investigated (*28*, *29*), but it has also been determined that the addition of tertiary amines, particularly pyridine and pyrazole, to the reaction mixture can produce an acceleration of the reaction, depending on the amine concentration (*29-31*). Rapid catalyst decomposition is observed at high concentrations of pyridine (*29*).

The most common procedure for making dialkylimidazolium salts involves the addition of an alkyl halide to *N*-alkylimidazole, yielding the dialkylimidazolium halide. A simple calculation reveals that only 2 mol% leftover imidazole, too small even to be seen in NMR spectra, leads to an imidazole concentration of approximately 0.16 M in the product ionic liquid. Depending on the [MTO] of the reaction, this relatively large amount of imidazole can lead to decomposition of the MTO catalyst to the inactive perrhenate.

The MTO/peroxide system is even more sensitive to halide contamination and especially to the presence of bromide (*32*, *33*). Most of the room-temperature ionic liquids are made by reacting *N*-alkylimidazole with an alkyl halide, forming the *N*-alkylimidazolium halide salt. The halide is then metathesized with the desired anion (e.g. BF_4^-, PF_6^-). Halides left over in the ionic liquids from the metathesis step compete with the olefinic substrate for oxidation in the catalytic cycle, Figure 4.

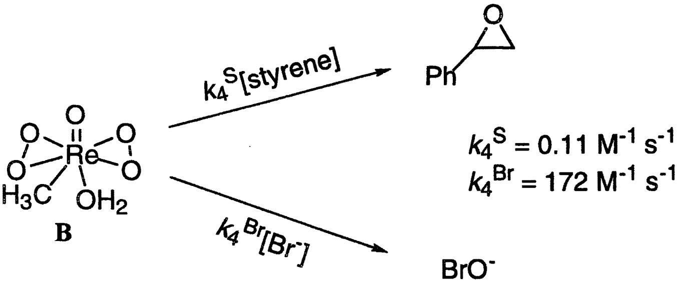
B
k_4^S[styrene]
k_4^{Br}[Br⁻]
Ph
BrO⁻
$k_4^S = 0.11\ M^{-1}\ s^{-1}$
$k_4^{Br} = 172\ M^{-1}\ s^{-1}$

Figure 4. Competing reactions of styrene and bromide with the diperoxorhenium complex.

As indicated by the rate constants given in Figure 4, the oxidation of bromide (*32*) occurs with a much higher rate constant than the oxidation of styrene (*22*). Bromide contamination is worse than chloride contamination because bromide is oxidized approximately 1400 times faster than chloride. Both bromide and chloride ions are oxidized by the peroxorhenium complexes

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to yield the hypohalite ions, which in turn form the hypohalous acids. The hypohalous acids can then effect the catalytic disproportionation of hydrogen peroxide to water and oxygen in the presence of excess hydrogen peroxide. Figure 5 illustrates the disproportionation cycle with bromide.

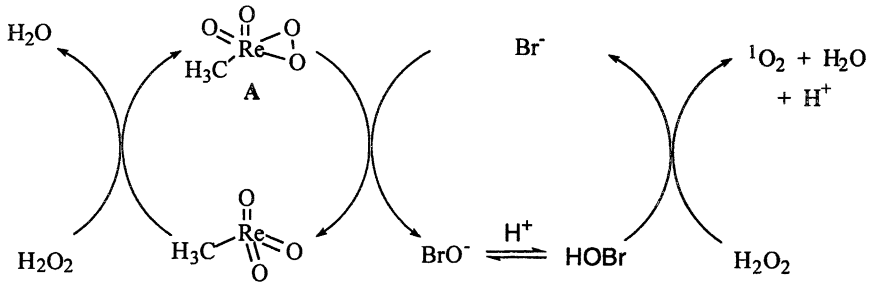

Figure 5. Catalytic Decomposition of H_2O_2 with Br^-, H^+, and the monoperoxorhenium complex.

In the presence of excess halide, the hypohalous acids react with the halide to form the diatomic halogen in solution, which halogenates the olefinic substrate.

$$\mathrm{HOBr} + \mathrm{H^+} + \mathrm{Br^-} \longrightarrow \mathrm{Br_2} + \mathrm{H_2O}$$

These reactions demonstrate clearly that care must be taken to remove traces of halide from the ionic liquid. Silver salts are generally the most effective reagents for metathesis, but an excess of Ag(I) in the ionic liquid will affect catalysis and, at sufficient concentrations, turn the ionic liquid brown upon exposure to light.

Comparative Kinetics of the MTO/Peroxide Reactions in [emim]BF_4

Kinetic data on reactions in ionic liquids are scarce; only electron transfer has been studied in any kind of kinetic detail (*34-37*). Here, we present some preliminary results of our study of the MTO/peroxide kinetics in [emim]BF_4.

The formation of the diperoxorhenium species, **B**, can be monitored using UV-vis, as **B** has a λ_{max} at 360 nm (ε = 1100 $L^{-1}mol\ cm^{-1}$). Figure 6 shows the spectrum of MTO and **B** in [emim]BF_4. The formation of **B** from **A** + H_2O_2 has a rate constant k_2 = 80 $M^{-1}\ s^{-1}$ in aqueous solution and 0.045 $M^{-1}\ s^{-1}$ in acetonitrile

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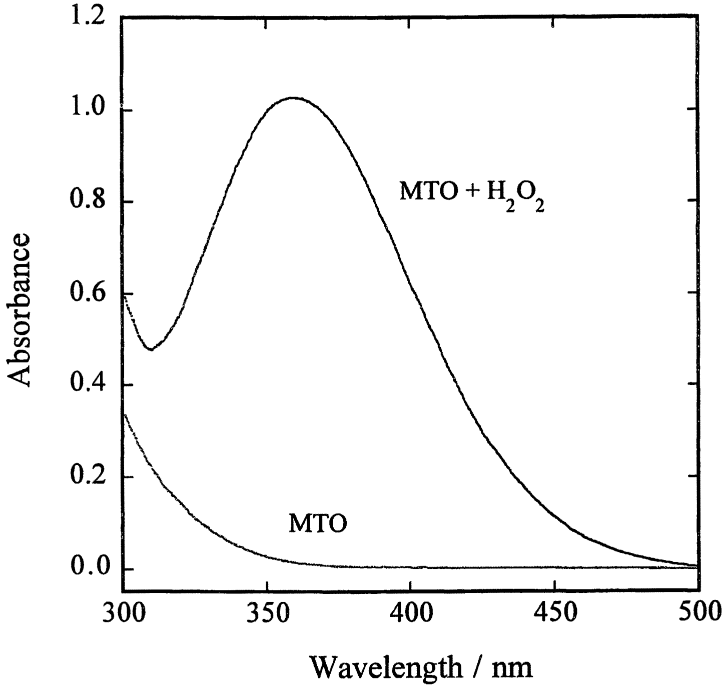

*Figure 6. UV-vis spectrum of MTO and **B** in [emim]BF_4. Conditions: 0.93 mM MTO, 42 mM H_2O_2, 0.1 M $HClO_4$.*

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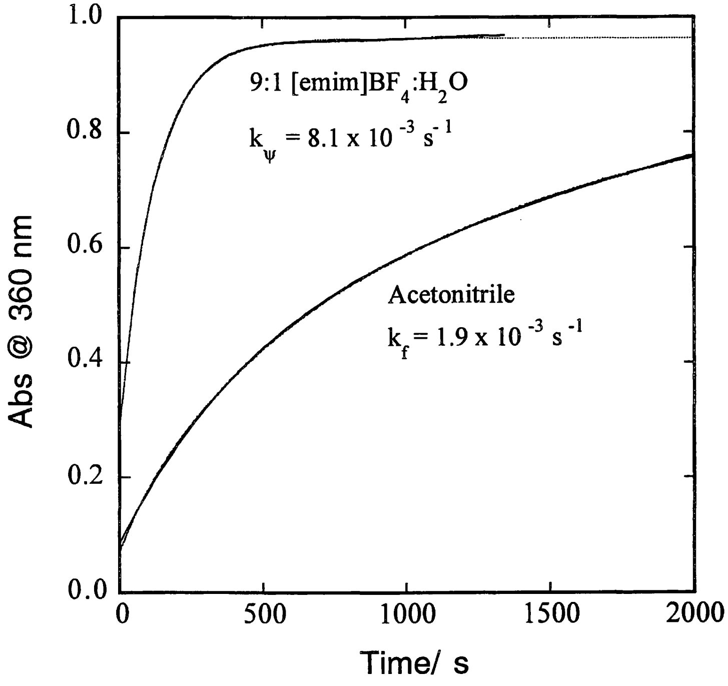

*Figure 7. Formation of **B** in [emim]BF_4 and CH_3CN.*

(*22*). The reaction in water is so fast that it can be measured quantitatively only by using stopped-flow kinetics, but the reactions in acetonitrile and in [emim]BF_4 can be monitored using conventional UV-vis. Typical kinetic traces for the formation of **B** in acetonitrile and in [emim]BF_4 are shown in Figure 7 (conditions: 0.1 M $HClO_4$, 0.93 mM MTO, 42 mM H_2O_2).

The first step of the reaction, the formation of **A**, is much faster in [emim]BF_4 than in acetonitrile. The second step is of the most interest. For the reaction in [emim]BF_4, the kinetic trace is fitted to a single exponential curve using least-squares fitting; for the acetonitrile reaction, the kinetic time profile must be fitted using a biexponential least-squares curve. As indicated by the pseudo-first-order rate constants, the formation of **B**, the second step, in 9:1 (v/v) [emim]BF_4:H_2O is approximately four times faster than in acetonitrile. The formation of **B** is clearly dependent on the water concentration of the medium, as the k_ψ under similar conditions with minimal water is approximately 5.1 x 10^{-3} s^{-1}, which is still more than twice as fast as in acetonitrile.

Studies watching the reaction of **B** with styrene under non-steady-state conditions yield rate constants for styrene oxidation that are practically identical to those obtained for the same reaction in acetonitrile. These two kinetics experiments indicate that [emim]BF_4 behaves less like a salt than does water. Our preliminary results validate the very recent report by Brennecke and Samanta which concludes that imidazolium- and pyridinium-based ionic liquids have polarities that fall between methanol and acetonitrile (*18*). In other words, the kinetic behavior of the MTO/peroxide system in [emim]BF_4 suggests that the solvent interactions, both between the cation and anion and between the solvent and solute, are not limited to Coulombic forces.

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Summary

Relatively little research has been conducted on catalytic oxygen-transfer reactions in ionic liquids, but the two examples given here suggest that catalytic oxidations have a future in these unique media. Both the (salen)Mn^{III}/ClO^- and the MTO/peroxide systems demonstrate that organic materials valuable as starting reagents for pharmaceuticals syntheses can be made cleanly in room-temperature, air- and water-stable ionic liquids. As the demand for cleaner technologies increases, the applications of benign oxidants, such as hydrogen peroxide, and non-volatile solvents are sure to gain more prominence in the chemical industry.

Acknowledgments

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Chapter 26

Transition-Metal-Catalyzed Hydrosilylation and Hydroboration of Terminal Alkynes in Ionic Liquids

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Abstract : Several ionic liquids have been studied as solvents for transition metal catalyzed hydrosilylation and hydroboration of terminal alkynes. Speier's catalyst has been used. In general, reactions are much faster in methyltrioctyl ammonium triflimide and β-*E* vinylsilanes were selectively obtained and isolated in good to excellent yields simply by bulb to bulb distillation. The solution of catalyst in ionic liquid could then be reused several times without loss of activity showing that recycling is an easy process. Lewis acidic chloroaluminate melts could also catalyze the hydrosilylation leading to Z-vinylsilanes and to some extent to polymerization of the starting alkyne. Rhodium and nickel (II) catalyzed hydroboration of terminal alkynes with pinacolborane was also studied. Wilkinson's catalyst in 1-butyl-3-methyl imidazolium chlorozincate at 40°C was shown to be the combination of choice for this reaction leading quantitatively to vinylboronates in less than two hours. Recycling of the zincate solution of rhodium catalyst could be realized with some lost of catalyst activity but with a significant increase of the regioselectivity. Nickel (II) gave regioselective hydroboration.

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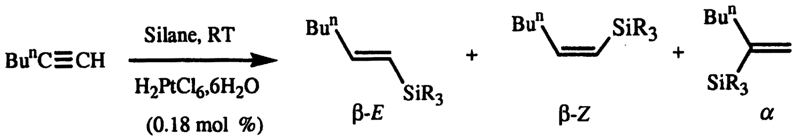
The role of ionic liquids (IL) as new green solvents is becoming more and more prominent. They seem to have a bright future as substitutes of conventional solvents in many fields including organic synthesis, catalysis, extraction etc...(*1-7*). They can disolve organic, organometallic and inorganic compounds and therefore are solvents of choice for the dissolution of transition metal catalysts. Their negligible vapour pressure, ease of handling and potential for recycling, circumvent many of the problems associated with volatile, molecular organic solvents. Also, their properties can be tuned by a proper choice of organic cation and its substitution, and inorganic anion as well. We herein report some of our work dealing with the transition metal catalyzed hydrosilylation and hydroboration of alkynes in ionic liquids. These two reactions belong to a family of additions to alkenes and alkynes known as hydrometallations including hydrostannation and hydrozirconation and others. Monohydrosilylation and monohydroboration of alkynes lead to vinylsilanes and vinylboranes respectively which are important synthetic intermediates (*8*). These reactions can be mediated by a variety of catalysts. The most commonly used are transition metal catalysts but several other possibilities including Lewis acids or radical initiators have been described (*9a*). It was expected that studying these catalyzed reactions in ionic liquids which are polar solvents would bring new insights into regio and stereoselectivities as well as reactivity. We also wanted to explore the possibility of catalyst recycling.

I - Catalytic Hydrosilylation of Monosubstituted Alkynes

I.a – Platinum catalyzed hydrosilylation of monosubstituted alkynes.

Hydrosilylation of alkynes is the most straightforward preparative method for vinylsilanes (*8-10*). This procedure can be radical induced providing mixtures of *cis-* and *trans-*hydrosilylation products. It was recently reported that Lewis acids such as $AlCl_3$ and $EtAlCl_2$ are very efficient catalysts for this reaction leading to *cis*-alkenyl silanes with very high regio- and stereoselectivities in good to high yields through a *trans*-hydrosilylation process(*11*). It is also well known that hydrosilylation is induced by transition metal catalysts. Among them, platinum catalysts are exceptionally efficient and can be used at concentrations of less than 1 ppm in various solvents. Two important classes of platinum catalysts may be used : those at the Pt° oxidation state like the Karstedt's catalyst (*12*) and those at higher oxidation states, particularly Pt^{IV}, e.g., Speier's catalyst, H_2PtCl_6 in isopropanol (*13*). In this preliminary work, we have chosen $H_2PtCl_6 . 6H_20$ as precatalyst dissolved in several ionic liquids for the hydrosilation of some monosubstituted alkynes including hex-1-yne, phenylacetylene and 2-methyl-1-buten-3-yne. A simple experimental protocol is as follows : under argon, in a Schlenk tube, Speier's catalyst, 5 mg (0.18 mol %), was dissolved in 1 ml of ionic liquid. 10 mmol (2 equiv.) of silane (Cl_3SiH, Me_2SiHCl or Et_3SiH) were then added and the reaction mixture stirred for 15 minutes. This was followed by the addition of 5 mmol (1 equiv.) of monosubstituted alkyne. Stirring was maintained for the appropriate time. Then the excess of the starting silanes and vinylsilanes were separated from the ionic liquid by bulb to bulb distillation under high vacuum (0.02 torr, temperature bath : 120°C). The remaining ionic liquid solution of catalyst was ready for another cycle without any further treatment. Results are reported in tables 1, 2, 3.

Table 1 : Hydrosilylation of hex-1-yne in ionic liquids at room temperature



Silane	Solvent (a)	Time (h)	% con-- version	Products β-E	β-Z	α	Yields % (b)
Cl_3SiH	CH_2Cl_2	4	100	90	0	10	85
	$[emim][NTf_2]$	9	100	95	0	5	94
	$[R_3NMe][NTf_2]$	1	100	95	0	5	95
	$[R_3NMe][Cl]^{(c)}$	No reaction	-	-	-	-	-
Me_2SiHCl	CH_2Cl_2	1	100	84	0	16	85
	$[emim][NTf_2]$	1	100	85	0	15	96
	$[R_3NMe][NTf_2]$	2	100	85	0	15	94
	$[R_3NMe][Cl]^{(c)}$	No reaction	-	-	-	-	-
Et_3SiH	CH_2Cl_2	4	100	93	0	7	85
	$[emim][NTf_2]$	8	100	85	0	15	95
	$[R_3NMe][NTf_2]$	2	100	90	0	10	95
	$[emim][BF_4]$	72	100	85	0	15	80

(a) $[emim]^+$ = 1-ethyl-3-methylimidazolium cation . $[NTf_2]^-$ = $[^{\theta}N(SO_2CF_3)_2]^-$; $[R_3Nme]^+$ = $[(CH_3(CH_2)_7)_3\ Nme]^+$

(b) Average isolated yields for 3 consecutive runs.

(c) Aliquat 336. Dried by phosgene treatment.

Average yields of isolated pure vinylsilanes are uniformly good in a 80-96 % range and are for three consecutive runs with the same catalyst solution. This shows the simplicity and the efficiency of this process. It should be noted that no reaction was observed in dried Aliquat 336. This might be the result of catalyst deactivation by the nucleophilic chloride anion. Another interesting

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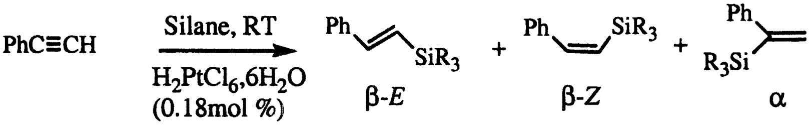
feature is the large solvent effect on the rate of the hydrosilylation with trichlorosilane in [emim][NTf_2] and [R_3NMe][NTf_2] : 9 hours and 1 hour respectively for the reaction to go to completion. β-*E* and α vinylsilanes were obtained in a 95/5 ratio comparable to results reported by Kumada et al. (*14*). With dimethylchlorosilane, reaction was over after one ([emim][NTf_2]) or two hours ([R_3NMe][NTf_2]) leading almost quantitatively to a 85/15 ratio of β-*E* and α-vinylsilanes. Triethylsilane was less reactive and reactions went to completion in about 12 hours at room temperature in [emim][NTf_2] and [R_3NMe][NTf_2] whereas it took 72 hours in [emim][BF_4] for a 80 % isolated yield. Purification of the products was very easily made either by bulb to bulb distillation of the crude reaction mixture. A solution of the catalyst in the ionic liquid was left back which could be used for another run without any further treatment.

Results for the hydrosilylation of phenylacetylene are reported in table 2.

Table 2 : Hydrosilylation of Phenylacetylene in ionic liquids at room temperature.



Silane	Solvent	Time (h)	% conversion	Products β-E	Products β-Z	Products α	Yields %[a]
Cl_3SiH	CH_2Cl_2	18	100	90	0	10	90
	[emim][NTf_2]	24	15	100	0	0	9
	[bmim][NTf_2]	24	100	100	0	0	82
	[R_3NMe][NTf_2]	1	100	100	0	0	95
Me_2SiHCl	CH_2Cl_2	0.5	100	98	0	2	92
	[emim][NTf_2]	48	100	94	0	4	95
	[bmim][NTf_2]	24	100	86	0	14	87
	[R_3NMe][NTf_2]	1	100	95	0	5	95
Et_3SiH	CH_2Cl_2	18	100	85	0	15	89
	[emim][NTf_2]	12	100	87	0	13	95
	[R_3NMe][NTf_2]	6	100	91	0	9	95
no solvent	[emim][BF_4]	36	100	85	0	15	90

(a) Average yields for 3 consecutive runs.

Trichlorosilane gave poor results in [emim][NTf_2], i,e 9 % yield, which we have been unable to improve whereas 100 % conversion and 82 % isolated yield

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of β-*E* vinysilane was obtained in [bmim][NTf_2]. Again, a large increase in the reaction rate was observed in the ammonium triflimide solvent where the reaction was over in less than one hour leading to an excellent 95 % yield of isolated product. The same observation holds for dimethylchlorosilane and triethylsilane. This might be the result of homogeneity of the reaction mixtures when [R_3NMe][NTf_2] was used as solvent. The regioselectivity of the addition also appeared to be dependant on the solvent and the silane. 100 % of the β-*E* vinylsilane was obtained with trichlorosilane as compared to a reported 69/31 mixture of β-E/α (*15*). Results for the hydrosilylation of 2-methyl-1-buten-3-yne are reported in table 3.

At room temperature, hydrosilylation of 2-methyl-1-buten-3-yne with trichlorosilane went to completion in one hour in [R_3NMe][NTf_2] leading exclusively to the β-*E* dienylsilane. No reaction was observed in [emim][NTf_2] for unknown reasons. A 90 % isolated yield could be obtained which has to be compared with 65 % after 6 h at 80°C by Licchelli et al (*16*) under conventionnal conditions. Results were more erratic with dimethylchlorosilane. The best results were obtained in [R_3NMe][NTf_2] leading to a 66 % isolated yield of the β-*E* dienylsilane. Partial polymerization of the starting enyne was also observed. Triethylsilane led to excellent results giving the β-*E* dienylsilane in 95 % yield. Nevertheless, regioselectivity was not complete and traces of the α-isomer were observed.

I.b - $AlCl_3$ catalyzed trans-hydrosilylation of hex-1-yne in chloroaluminate melts.

$AlCl_3$ and $EtAlCl_2$ catalyzed hydrosilylation of alkynes has recently beendescribed by Yamamoto et al. (*11*) as a very efficient way to prepare β-*Z* vinylsilanes. This suggested to us to use acidic chloroaluminate melts as solvents for the hydrosilylation of terminal acetylenes. One major advantage of this method would be that an aqueous work up is not necessary to isolate the reaction products. Some attemps have been made to perform hydrosilylation of hex-1-yne in chloroaluminate ionic liquids. Preliminary results are reported in table 4.

This reaction appeared to be difficult to control and experimental conditions have to be improved. Positive results were only observed for [bmim][Cl]/$AlCl_3$ = 1/1.2. After 45 minutes of reaction with Et_3SiH, the β-*Z* vinylsilane was obtained together with polymers. It could be isolated in a 50 % yield by bulb to bulb distillation and the chloroaluminate ionic liquid reused for another run. Polymerisation of the alkyne became the prominent reaction with dimethylchlorosilane and the sole reaction observed when trichlorosilane was used. So, it seems that a certain Lewis acidity must be reached to promote the reaction but, meanwhile, it also induces polymerization of the alkyne. More

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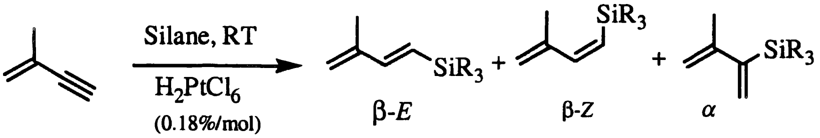
Table 3 : Hydrosilylation of 2-methyl-1-buten-3-yne in ionic liquids at room temperature.



Silane	*Solvent*	*Time (h)*	*% conversion*	*Products*			*Yield %*[(a)]
				β-E	*β-Z*	*α*	
Cl_3SiH	$[emim][NTf_2]$	No reaction		-			
	$[R_3NMe][NTf_2]$	1	100	100	0	0	90
	no solvent	6 (80°C)	100	100	0	0	60 [(b)]
Me_2SiHCl[(c)]	$[emim][NTf_2]$	24	60-30	100	0	0	17
	$[R_3NMe][NTf_2]$	30	80	100	0	0	66
	$[bmim][NTf_2]$	30	90-70	100	0	0	48
	$[emim][BF_4]$	15	100	100	0	0	16
	no solvent	6 (80°C)	100	100	0	0	80 [(b)]
Et_3SiH	$[emim][NTf_2]$	24	100	93	0	7	95
	$[R_3NMe][NTf_2]$	20	100	95	0	5	95
	$[bmim][NTf_2]$	50	100	95	0	5	90
	$[emim][BF_4]$	72	80	95	0	5	75

(a) Yields are for pure isolated compounds. Given numbers are an average of 3 consecutive reactions with the same catalyst solution. (b) ref. 16. (c) Some polymerization occurred with this silane.

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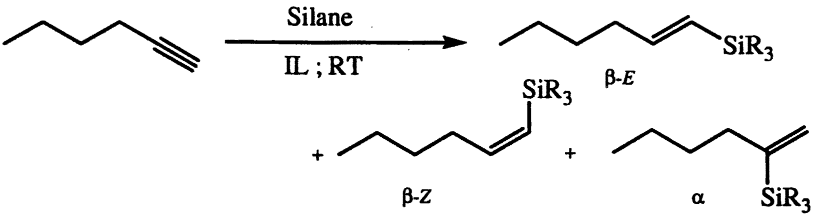
Table 4 : Hydrosilylation of hex-1-yne in chloroaluminate IL at room temperature.



Silane	*X in [bmim][Cl], XAlCl₃*		*Time(h)*	*Conver-sion*	*Products βZ/βE/α*	*Yield %*
Et_3SiH	[bmim] [Cl]	1.1	24	No reaction	-	-
	[bmim] [Cl]	1.2	45min	100	100/0/0 (+ polymers)	>50[a]
	Toluene (0°C)	0.2	1 h	100	100/0/0	90[b]
Me_2SiHCl	[bmim] [Cl]	1.1	24	No reaction	-	-
	[bmim] [Cl]	1.2	2min	100	(c)	15[a]
Cl_3SiH	[bmim] [Cl]	1.1	24	No reaction	-	-
	[bmim] [Cl]	1.2	5min	100	Polymer	-

[a] yields are for isolated pure compounds (average value for 3 runs). [b] reaction performed with 1-dodecyne (réf. 11). [c] Regio and stereo selectivities were variable. Polymers were also formed.

studies have obviously to be done to better understand and optimize the reaction conditions. Nevertheless, the simplicity of the methodology and the possibility of recycling are worthy of note.

II - Catalytic Hydroboration of Monosubstituted Alkynes with Pinacolborane

The hydroboration of alkynes is a well documented reaction providing a very general route to vinylboranes which are important synthetic intermediates (*17,18,19,20*). Dialkoxyboranes such as catecholborane and pinacolborane (PinBH) are rather sluggish hydroboration reagents which necessitate the use of excess reagent and thermal activation. Transition metal catalyzed hydroboration of olefins with catecholborane and pinacolborane has greatly extended the scope of the use of these boranes and this methodology has proven to be complementary to the uncatalyzed reaction. However, much less is known about the catalyzed hydroboration of acetylenes with catechol borane : rhodium(*21*) and nickel (II) (*22*) catalysts have been studied. $NiCl_2$(dppe) (1 mol %) catalyzed the hydroboration of hex-1-yne and phenylacetylene with catecholborane at room temperature in THF leading to the corresponding boronic esters in good yields (*23*).

Pinacolborane (PinBH), a stable, easy to prepare dialkoxyborane (*24*) has been shown to hydroborate alkynes using either rhodium or nickel catalysts (*25*) leading to easily purified and stable vinylboronates. Zirconium catalyst (Cp_2ZrHCl) has also been used (*26*). We have studied the hydroboration with PinBH of hex-1-yne, phenylacetylene and 2-methyl-1-buten-3-yne in various ionic liquids without catalyst and in the presence of Wilkinson's catalyst ($RhCl(PPh_3)_3$) and $NiCl_2$(dppe). The reaction of PinBH with hex-1-yne at room temperature in various ionic liquids and CH_2Cl_2 for comparison has been first studied. Results are reported in table 5.

The products were isolated by a simple bulb to bulb distillation from the crude reaction mixture. The ionic liquid solution of catalyst which is left after this operation can be reused without any further treatment.

Examination of the results reveals that the reaction is slower in IL than in CH_2Cl_2, isolated yields being in the same range except for the zincate [bmim][Cl]/$ZnCl_2$ (1:1) where an 82 % yield was obtained. Note also that regioselectivity is complete giving exclusively the β-*E* vinylboronate in all solvents without catalyst (entries 1, 4, 7, 10, 13, 16). In the presence of 1.2 mol % of Wilkinson's catalyst, reaction times are shorter and isolated yields identical or better than without catalyst. Nevertheless, a significant loss of regioselectivity was observed, i.e. usually a 4/1 β/α ratio (entries 2, 5, 8, 11, 14,

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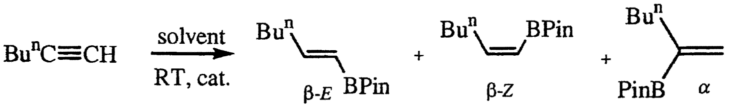
Table 5 : Catalyzed or non catalyzed hydroboration of hex-1-yne with pinacolborane in IL [(a)]



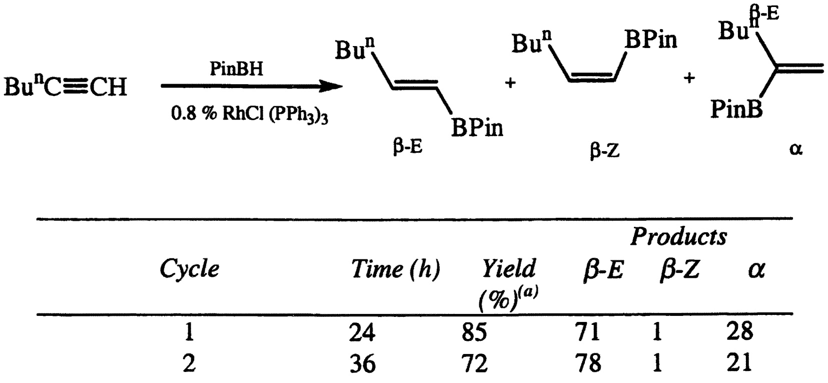
Entry	*Solvent*	*Cat.*	*Time (h)*	*Yield (%)* [(b)]	*β-E*	*β-Z*	*α*
1	CH_2Cl_2	-	48	58	100	0	0
2	"	A [(c)]	24	97	82	2	16
3	" [(d)]	B [(e)]	48	60	100	0	0
4	$[R_3NMe]$ NTf_2 [(f)]	-	144	43	100	0	0
5	"	A	48	55	82	0	18
6	"	B	72	77	98	0	2
7	[bmim][Cl]/$AlCl_3$ (1:0.8)	-	72	63	100	0	0
8	"	A	48	55	86	0	14
9	"	B	72		No reaction		
10	[bmim][Cl]/$AlCl_3$ (1:1)	-	72	66	100	0	0
11	"	A	24	66	80	0	20
12	"	B	72	47	100	0	0
13	[bmim][Cl]/$AlCl_3$ (1:1.1)	-	72	61	100	0	0
14	„	A	48	70	82	7	11
15	"	B	72	74	100	0	0
16	[bmim][Cl]/$ZnCl_2$ (1:1)	-	120	82	100	0	0
17	„	A	48	77	83	1	16
18	„	B	48	81	96	0	4

(a) 2 equivalents of PinBH were used. (b) Isolated yields after bulb to bulb purification. (c) 1.2 mol % of RhCl $(PPh_3)_3$. (d) 81 % yield of pure β-E in THF at RT in 3 h (*23*). (e) 1.2 mol % of $NiCl_2$ (dppe). (f) $R_3NMe = [CH_3(CH_2)_7)_3NMe$.

17). Some β-*Z* vinylboronate was also formed, up to 7 % in the case of the acidic chloroaluminate melt (entry 14) with nickel catalyst. The hydroboration reaction was usually slower than in the presence of the rhodium catalyst but selectivities are much better leading almost exclusively to the β-*Z* vinylboronate (*25*). In several cases, isolated yields were also better (entries 6, 15, 18), the chlorozincate melt being an interesting and efficient solvent for this reaction (entry 18).

It is interesting to note that no reaction occurred in the basic IL [bmim][Cl]/$AlCl_3$ (1:0.8) most probably because of the interaction of chloride anion with the nickel (II) complex leading to $NiCl_4$ species (*27*) which are not active. In all these reactions, one important point is recycling of the catalyst solution. The rhodium catalyzed reaction in [bmim][Cl]/$AlCl_3$ (1:0.94) has been chosen for this study and results are reported in table 6.

Table 6 : Rhodium catalyzed hydroboration of hex-1-yne at RT in [bmim][Cl]/$AlCl_3$ (1:0.94). Recycling of the catalyst.



Cycle	Time (h)	Yield (%)$^{(a)}$	Products		
			β-E	*β-Z*	*α*
1	24	85	71	1	28
2	36	72	78	1	21
3	48	67	87	3	10
4	48	59	91	2	7

(a) Isolated yields. Products were purified by bulb to bulb distillation under vacuum at 80°C. The IL solution of catalyst was then reused without any further treatment.

There are two important observations that must be pointed out. First, reaction time increased with the number of recyclings with a concomittent decrease in isolated yields as can be seen when comparing cycles 1 and 4. Second,regioselectivity changed very much with the number of cycles going from a β-E/α = 71/28 ratio to a 91/7 ratio. The reason for that is unknown at the moment and more work has to be done to understand. Nevertheless, the possibility of recycling the catalyst solution has been established.

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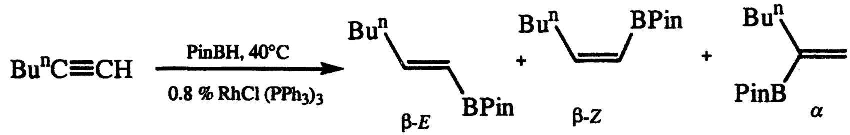
Recycling of the rhodium catalyst solution has also been studied in [bmim][Cl]/$ZnCl_2$](1:1) at 40°C instead of room temperature since these conditions have been shown to give better yields. Results are reported in table 7.

Table 7 : Rhodium catalyzed hydroboration of hex-1-yne at 40°C in [bmim][Cl][$ZnCl_2$]. Recycling of the rhodium catalyst.



Cycle [(a)]	Yield (%) [(b)]	Products β-E	β-Z	α
1	83	80	5	15
2	76	82	2	16
3	73	85	1	14
4	72	91	0.5	8.5
5	55	93	0.5	6.5
6	44	95	0.5	4.5

(a) Reaction time : 1.5 h.

(b) Isolated yields. Products were purified by bulb to bulb distillation under vacuum at 80°C and the IL solution of catalyst reused without any further treatment.

The first important feature to point out is the dramatic effect of temperature on the reaction rate : at room temperature, 48 hours were necessary for the reaction to go to completion (see table 5) as compared to 1.5 h at 40°C. Isolated yields and regioselectivity were comparable. One reason for that might be the large difference in viscosity of the reaction mixture at room temperature and at 40°C. At this temperature, the chlorozincate melt is very fluid and stirring easy whereas at room temperature, this IL is very viscous. Secondly, recycling the catalyst solution was also possible with this IL. But after 6 runs, yield after 1.5 hour of reaction was only 44 % showing a desactivation of the catalyst solution for unknown reasons at this time. Also, regioselectivity and stereoselectivity increased very much going from a ratio β-*E*/β-*Z*/α = 80/5/15 at the first run to 95/0.5/4.5 at the sixth one. These interesting points are under active investigation.

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Conclusion

This preliminary work clearly shows that ionic liquids are very valuable solvents to perform transition metal catalyzed hydrosilylation and hydroboration of terminal alkynes. This also holds for alkenes (*28*). Important solvent effects were observed impacting rates of reaction and selectivities. For example, methyltrioctylammonium triflimide was shown to be the solvent of choice for the platinum catalyzed hydrosilylation giving the higher rates for the hydrosilylation reaction and the best regio and stereoselectivities. This might be due to the homogeneous character of these reaction mixtures. Very high yields and regio and stereoselectivites could be achieved. Recycling of the solution catalyst could be realized without loss of activity. Hydrosilylation was also possible in acidic aluminum melts leading exclusively to the β-Z vinylsilane with Et_3SiH also in moderate isolated yields due to polymerization problems. Nevertheless, this work opens the way to an interesting way of producing Z-vinylsilanes. The best solvent for rhodium catalyzed hydroboration with pinacolborane was found to be 1-butyl-3-methylimidazolium chlorozincate at 40°C where the hydroboration was over in 1.5 hours. The slightly basic aluminum melt [bmim][Cl]/$AlCl_3$ (1:0.94) was also found to be a good solvent for this reaction. In agreement with literature data, $NiCl_2$(dppe) catalyzed hydroboration was shown to be the more selective reaction leading almost exclusively to the β-E vinylboronates. Reactions are slower than when catalyzed by Wilkinsons' catalyst. Recycling of the solutions catalyst has been shown to be easily realized also with some lost of yields but an increase in selectivities. A number of questions were raised that we cannot answer to at the moment and which points out our deficiency in knowledge of these new solvents and understanding the chemistry occuring in them.

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Chapter 27

Application of Room-Temperature Ionic Liquids in Biocatalysis: Opportunities and Challenges

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Biocatalysis is now a key technology in the synthesis of chiral pharmaceuticals and agrochemicals. In order to deal with the low aqueous solubility of many substrates, biocatalytic processes are frequently performed in organic media to facilitate conversions at higher overall concentrations. This poses problems, however, since organic solvents are known to damage bacterial cell membranes and promote enzyme denaturation. Recent work has established that ionic liquids can successfully replace organic solvents in a range of whole cell and isolated enzyme bioconversions. In most examples studied to date, reaction rates and yields are comparable to, or greater than, those obtained in previously optimised organic systems. Significant enhancements in biocatalyst stability have also been observed. This chapter reviews the opportunities for using ionic liquids in biocatalytic processes and outlines key research themes that remain to be addressed. In particular the potential of ionic liquids as "designer solvents" for bioconversions will be described.

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

Introduction

Biocatalysts are now finding increasing use in the production of chiral synthons in the pharmaceutical, agrochemical and fine chemical sectors. This is because they posses a number of significant advantages over chiral chemical catalysts which include; high stereo-, regio- and positional-specificity, high atom efficiency (due to the avoidance of protection and deprotection steps) and the ability to operate under mild conditions. They catalyse a wide range of chemical transformations useful in synthetic organic chemistry such as redox reactions and carbon-carbon bond formation in addition to well established hydrolysis and esterification reactions (*1,2*).

A toolbox of recombinant DNA techniques also exists which can greatly enhance biocatalyst activity (initial rate of conversion) and stability (activity over time). These include the ability to clone and overexpress enzymes in particular hosts (*3*), to rationally engineer metabolic pathways (*4*) and to artificially evolve enhanced specificity (*5*). As a result, the costs of biocatalysts and chiral chemical catalysts are now comparable (*6*) and it is estimated that over two hundred biocatalytic processes have been operated commercially (*7*).

In Nature, biocatalysts have evolved to work in an aqueous environment. For industrial bioconversions, however, many of the substrates and/or products of interest have low aqueous solubilities or water may be a product of the transformation. These can lead to unacceptably low space-time yields or degrees of conversion (yield of product on substrate). This, in turn, has lead to the development of bioconversions operated in 'non-conventional' media, usually an organic solvent or a water-solvent biphasic mixture, in order to effect bioconversions at higher overall concentrations (*8*).

Biocatalysis in 'Non-conventional' Media

Biocatalysts come in two major forms either whole microbial cells or isolated enzymes (*1*). The first record of a biocatalyst functioning in the presence of an organic solvent appeared in the 1930's (*9*). It was over 40 years later, however, that the industrial potential of the technology was realised with key publications on cholesterol modification in aqueous-organic biphasic media by whole *Nocardia* cells (*10*) and the realisation that enzymes could function in anhydrous, or nearly anhydrous, organic solvents (*11*). The primary benefits of using organic media are the solubilisation of higher concentrations of poorly water-soluble substrates and/or products, control of substrate and product partitioning (to overcome inhibitory or toxic effects) and the ability to shift reaction equilibria toward product formation (*8, 12*). Other benefits might be the suppression of undesirable hydrolyses and easier product recovery.

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Based on the form of the biocatalyst used and the quantity of aqueous phase present it is possible to distinguish four main reaction systems when considering biocatalysis in 'non-conventional' media. These are shown schematically in Figure 1. In each case the biocatalyst may be free or immobilised which, in the case of isolated enzymes, converts them into an insoluble form. The single liquid-phase systems may contain small amounts of added water (typically < 5% v/v) or be totally anhydrous. Other, more specialized, reaction media also exist such as those involving liquid/supercritical CO_2 (*13*). When considering organic solvents as the non-aqueous medium, there are published examples of bioconversions occurring in each of the four identified systems. In many cases significant improvements in space-time yields have been reported compared to transformations conducted in entirely aqueous media (*8*, *12*). Rules have also been developed to enable the rational selection of solvents for use with particular biocatalysts and transformations (*14*, *15*).

The use of organic solvents, however, raises a number of separate issues. The main concerns are their toxicity to both process operators and the

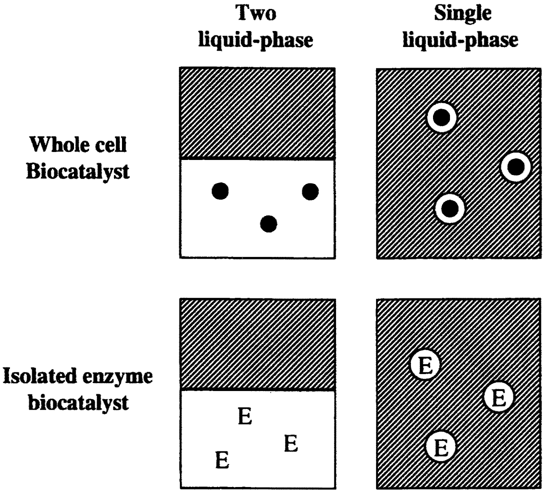

Figure 1. Schematic representation of the various reaction systems possible when considering biocatalysis in 'non-conventional' media; (●) whole cell biocatalyst, (E) isolated enzyme biocatalyst. Hashed phases represent organic solvent or ionic liquid media. Based on reference 8.

environment, and the volatile and flammable nature of most organic solvents that make them a potential explosion hazard (*16*). Organic solvents have also been shown to damage the membranes and cell walls of bacterial biocatalysts reducing their long-term operational stability. This has led to considerable work on understanding solvent effects and the development of solvent-tolerant bacteria (*17*). Similarly, exposure to aqueous-organic interfaces can lead to denaturation of enzyme biocatalysts as can their suspension in organic media. The use of room temperature ionic liquids as replacements for organic solvents in biocatalytic processes could potentially overcome many of these issues and open up some exciting new opportunities.

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Structure and Properties of Room Temperature Ionic Liquids

Ionic liquids, also known as molten salts, are solutions composed entirely of ions. Originally discovered in 1913, a wide range of room temperature ionic liquids have since been synthesised that are stable under ambient conditions and in the presence of air (*18, 19*). Recently there has been considerable interest in ionic liquids as media for clean organic synthesis (*19*). A wide variety of chemical transformations have now been performed in ionic liquids such as alkylation reactions, Diels-Alder cyclisations and Heck coupling reactions. In many cases significant yield improvements, compared to reactions carried out in conventional organic solvents, have been observed (*21*).

The physicochemical properties of ionic liquids are summarized in Table I. The most widely used to date are probably 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6], and 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF_4]. In both cases the cation, [bmim], is large compared to simple inorganic cations which accounts for their low melting point and relatively low viscosity at ambient temperature. [bmim][PF_6] is water immiscible while [bmim][BF_4] is water miscible. Most ionic liquids exhibit a high solubility for many organic molecules typical of those used in biocatalytic applications. The polarity of [bmim][PF_6], for example, is thought to be greater than that of acetonitrile but less than methanol (*22*).

Due to their non-volatile (virtually zero vapour pressure) and non-flammable nature, ionic liquids could provide a more 'green' and safe alternative to the use of organic solvents in bioconversion processes. Of particular interest is the ability to readily alter the physicochemcial properties of these solvents by simple structural modifications to the cations or changes in anion (*19*). This offers the opportunity to design an ionic liquid optimised for a particular process *i.e.* they have the potential to be considered "designer solvents" (*23*). With up to 10^{18}

different ionic liquids capable of being prepared (K. Seddon, personal communication) this offers a continuum of solvent properties.

Table I. The Interest in Ionic Liquids for Application to Biocatalysis in 'Non-conventional' Media. Compiled from References 19 and 20.

Properties of Room Temperature Ionic Liquids
Non-volatile, non-flammable, low toxicity
Liquid and stable over a wide temperature range (typically -80 °C to 200 °C)
Relatively low viscosity with Newtonian rheology
Non-corrosive and compatible with common materials of construction
Good solvents for many organic, inorganic and polymeric materials
Immiscible with a wide range of organic solvents
Immiscible (or miscible) with water
Able to suppress solvation and solvolysis phenomena
Tunable physicochemical properties ("designer solvents")

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Examples of Biocatalysis Using Ionic Liquids

The feasibility of using ionic liquids as media in which to conduct biocatalytic reactions was established in a series of publications between July and December 2000 (*20, 24, 25*). Here we review these and later works and also show that a whole cell biocatalyst can function in a single liquid-phase ionic liquid system. The work is presented according to the classification of reaction systems shown in Figure 1 though to date there is no published example of an isolated enzyme transformation occurring in an aqueous-ionic liquid biphasic system.

Two Liquid-Phase, Whole Cell Systems

The first publication on the use of a whole cell biocatalyst in a biphasic aqueous-ionic liquid system examined the hydration of poorly water-soluble aromatic dinitriles (*20*). This work used cells of *Rhodococcus* R312 to catalyse the transformation of 1,3-dicyanobenzene (1,3-DCB) to 3-cyanobenzamide (3-CB) and 3-cyanobenzoic acid (3-CA). Both conversions are part of the nitrile degradation pathway of the *Rhodococci* and involve the successive action of a nitrile hydratase and an amidase enzyme respectively (*26*). The synthetic applications of this enzyme system are well known as is the ability of the nitrile

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hydratase to perform regio- and stereo-selective transformations of a range of aromatic and heterocyclic substrates (*27, 28*).

The design and operation of two-phase biocatalytic processes has recently been reviewed (*29*). As in the majority of cases, a biphasic system was used in this work to allow dissolution of higher concentrations of the substrate, 1,3-DCB, and to control the level of substrate partitioning into the conjugate aqueous phase (*30*). The results in Figure 2 show that similar biotransformation profiles were obtained in both aqueous-toluene and aqueous-[bmim][PF_6] systems (these were performed at the same initial substrate concentration of 1 g l^{-1} which is close to the solubility limit of 1,3-DCB in this particular ionic liquid). Most interesting, however, is the relative decrease in the rate of acid formation in the ionic liquid medium since production of the amide product is often favoured from the point of view of subsequent chemical modification (*27*). Further experiments also showed considerably enhanced stability of the *Rhodococcus* R312 cells in the aqueous-[bmim][PF_6] system (*20*).

Single Liquid-Phase, Whole Cell Systems

Most recently we have examined the *Rhodococcus* R312 catalysed transformation of 1,3-DCB in a single phase [bmim][PF_6] system. As shown in Figure 3 the cells remain active and the rate of conversion is a function of the amount of water present. In this case the concentration of 3-cyanobenzoic acid was determined by HPLC (*20*) after rapid removal of the cells (filtration through a 0.2 μm membrane) and extraction of the product into phosphate buffer at pH 7. The amide concentration could not be accurately determined due to an unidentified compound in the aqueous extract that eluted at a similar retention time. While the rate of transformation is slower than in the biphasic systems studied previously, a similar degree of conversion of the 1,3-DCB into 3-cyanobenzoic acid was observed.

Although the generality of our findings with the *Rhodococcus* system needs to be established, they do suggest that ionic liquids have no overly adverse effect on the structure and function of bacterial cell membranes or that they are inherently toxic. Microscopic examination of the cells after exposure to [bmim][PF_6] showed no evidence of lysis although some clumping together was observed in the single phase ionic liquid. Cells plated out on nutrient agar following the bioconversion were found to still be viable.

Single Liquid-Phase, Isolated Enzyme Systems

The use of isolated enzyme biocatalysts in single liquid-phase ionic liquids is the most developed area of research to date. The first example to appear was the thermolysin catalysed synthesis of the artificial sweetener Z-aspartame as shown in Figure 4 (*24*). Working with [bmim][PF_6] containing 5% v/v water, Russell and co-workers found comparable rates and yields to the same reaction performed in relatively polar organic solvents such as ethanol and *tert*-amyl alcohol. As with our work on whole cell biocatalysts, enhanced stability of the thermolysin was also observed.

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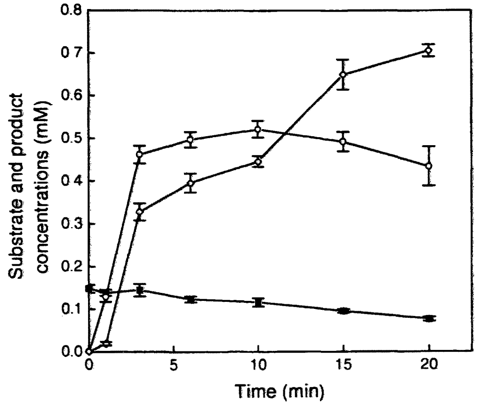

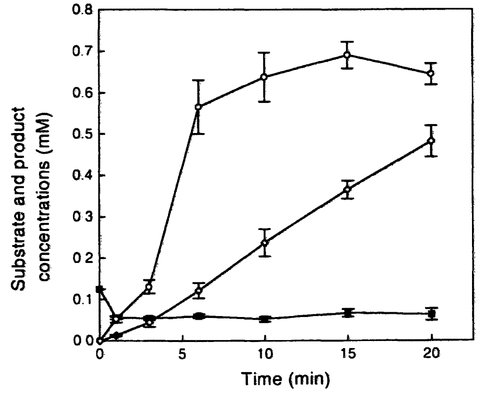

Figure 2. Rhodococcus *R312 catalyzed transformation of 1,3-DCB in (top) an aqueous-toluene two-phase system and (bottom) an aqueous-[bmim][PF$_6$] two-phase system. Aqueous phase concentrations of (■) 1,3-DCB, (○) 3-CB, (◊) 3-CA. Biocatalyst = 100 g$_{ww}$ l^{-1} of aqueous phase (pH 7), phase ratio = 0.2 v/v, initial 1,3-DCB concentration in toluene or [bmim][PF$_6$] = 1 g l^{-1}. Reprinted by permission of Wiley-Liss Inc., a subsidiary of John Wiley and Sons Inc., from reference 20. Copyright 2000 John Wiley & Sons Inc.*

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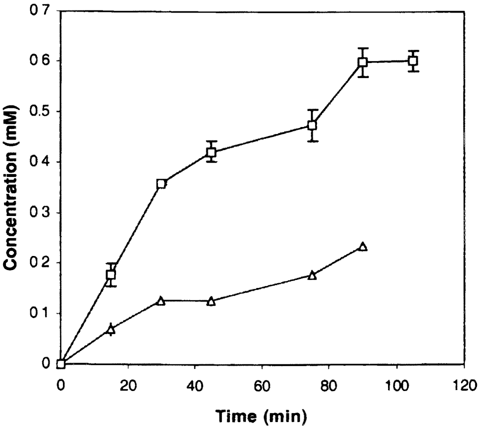

Figure 3. Rhodococcus *R312 catalyzed transformation of 1,3-DCB in [bmim][PF$_6$]. Production of 3-cyanobenzoic acid with (□) 9.0% v/v added water and (Δ) 4.5% v/v added water. Biocatalyst = 90 g_{ww} l^{-1}, initial 1,3-DCB concentration = 1 g l^{-1}.*

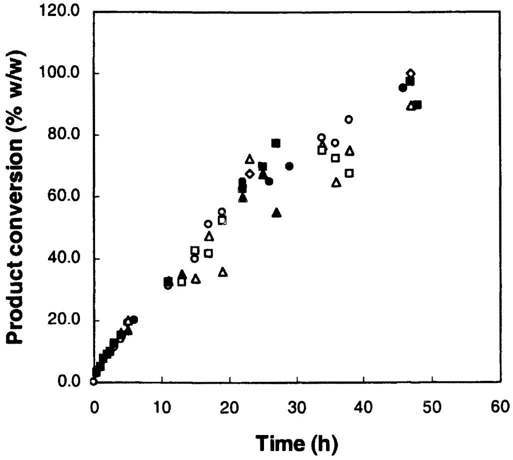

Figure 4. Thermolysin catalysed synthesis of Z-aspartame in [bmim][PF_6] using fresh (solid symbols) and recycled (open symbols) ionic liquid. Biocatalyst = 10 g l^{-1}, carbobenzoxy-L-aspartate = 20 mM, L-phenylalanine methyl ester hydrochloride = 100 mM, added water = 5.0% v/v. Adapted with permission from reference 24.Copyright 2000 American Chemical Society and American Institute of Chemical Engineers.

The first example of an enzyme working in a totally anhydrous ionic liquid phase was subsequently performed by Sheldon and co-workers (*25*). Using both free and immobilised forms of *Candida antarctica* lipase B (Novozym 435), they successfully demonstrated a range of synthetically useful reactions such as alcoholysis, ammonolysis and perhydrolysis. Experiments were performed in [bmim][BF_4] and/or [bmim][PF_6] with rates and yields being comparable, or better, to those obtained in previously optimised organic solvent systems.

Most recently Kragl and co-workers have shown the potential of ionic liquids to become the "designer solvents" of the future (*31*). Working with a range of ten different ionic liquids they examined the dynamic kinetic resolution of 1-phenylethanol by a lipase catalysed transesterification with vinyl acetate. The transformations again showed similar kinetics and yields to reactions performed in organic solvents. More interesting, however, was the fact that in certain cases the enantiomeric excess of the desired product was enhanced. This is the first concrete example of the interaction between an ionic liquid and an enzyme altering the selectivity of a biocatalytic reaction. The same group has also reported work on the β-galactosidase catalysed synthesis of *N*-acetyllactosamine using 25% v/v [mmim]$MeSO_4$ as a co-solvent (*32*).

Even at this early stage, the above examples would tend to suggest that enzyme catalysis in ionic liquids is a generic feature amongst various structural classes of proteins. What is not so clear, however, is the relationship between the state of the enzyme in the ionic liquid, either dissolved or in suspension, and its activity as conflicting reports appear to exist (*24, 25*). This may be due to the differing amounts of water present in the ionic liquid preparations used.

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Future Research Priorities

The potential of ionic liquids in bioconversion processes is immense however a number of issues remain to be addressed if this potential is to be fulfilled. These relate to the basic science involved (Table II) together with a number of engineering and industrial concerns (Table III).

Crucial to the control and optimisation of biological catalysis will be an understanding of how ionic liquids interact with the structure and function of isolated enzymes. The role of water in this regard also needs to be determined. Only if a rational basis for these interactions can be elucidated will the idea of using ionic liquids as "designer solvents" become a reality and the need to screen many ionic liquids for each new application avoided. Similar considerations apply to the influence of ionic liquids on the cell membranes of bacterial systems. More data is clearly needed for a range of microorganisms with different physiology, *e.g.* Gram positive and Gram negative bacteria, and a suitable toxicity scale, such as the Log P scale for organic solvents (*14*), needs to be defined.

Table II. Basic Science Issues to Address

Whole Cell Biocatalysis	*Isolated Enzyme Biocatalysis*
Generality of results to date	Generality of results to date
Membrane structure and function	Structure and dynamics
Role of water	Mechanism and kinetics
Definition of toxicity scale	"Memory effects"
Effect on intracellular enzymes	Role of water
Stability	Stability
	Reaction equilibria

Table III. Engineering and Industrial Issues to Address

Biochemical Engineering	*Industrial and Regulatory*
Mixing and phase separation	Cost and supply
Diffusion and mass transfer	Safety and toxicity
Product recovery	Long term stability
Ionic liquid selection criteria	Disposal
Design and optimisation	Regulatory approval
Cleaning and recycling	

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A key issue in terms of processing is product recovery from ionic liquid phases although a number of possibilities have now been demonstrated. Quantitative recovery of biocatalysis products from [bmim][PF_6] has been achieved by ourselves (this work) and others by liquid-liquid extraction with water (*24*) or organic solvents (*25*) and from [bmim]$(CF_3SO_2)_2N$ by vacuum distillation (*31*). This has allowed recycling of the ionic liquid and biocatalyst over 3-5 cycles (*24, 31*). Other potential product recovery techniques include extraction with liquid or supercritical CO_2 (*13, 33*) or solid-phase adsorption. A greater understanding of the relationship between the structure of an ionic liquid and key physicochemical properties, such as density, viscosity, heat capacity and thermal conductivity, will also aid the rational design of biocatalytic reactors and product recovery operations.

Major industrial concerns are still the lack of precedent in the use of ionic liquids, their bulk commercial availability and data on their long term stability and toxicity. Recycling and disposal of ionic liquids also need to be addressed. Crucial to the pharmaceutical sector will be regulatory approval of their use and validation of their removal from the final dosage form of the product.

Conclusions

In a relatively short period of time the potential of performing both whole cell and isolated enzyme catalysed bioconversions in ionic liquid media has been established. Most surprising was the way in which independent groups around the world separately examined the majority of the reaction systems that could be envisaged for their use. Future work will establish how generic this phenomenon really is and should aim towards a level of understanding that allows the rational optimisation of processes exploiting the unique properties offered by ionic liquids.

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Chapter 28

Room-Temperature Ionic Liquids as New Solvents for Carbohydrate Chemistry: A New Tool for the Processing of Biomass Feedstocks?

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Room-temperature ionic liquids (RTILs) can be used as reaction media for carrying out chemical reactions with carbohydrates. This study focused on simple acetylation reactions of partially protected as well as 'free' sugars, and it was shown that the choice of RTIL determines the efficiency of these transformations.

The production of chemicals, fuels and materials from renewable resources such as lignocellulosic biomass is gaining increased attention from the global research community (*1*). Aside from the complex geopolitical issues associated with the mining of fossil resources such as petroleum and coal, these particular non-renewable carbon feedstocks have become the center of discussions around 'global warming' that is said to be caused by the build-up of carbon dioxide emissions. On the other hand, many countries produce vast supplies of agricultural by-products that are not marketable and that thus must be disposed of as 'waste' materials. This usually involves combustion to generate process heat, or use in low-value applications such as soil improvement. A significant goal of the biomass processing industry is to upgrade the value of many agricultural products through chemical conversion methods that can modify or even improve the physical and/or chemical properties. However, this also introduces a major challenge in that biomass feedstocks are much more complex in their chemical and structural composition, and conventional chemical processes are not easily adapted to process these raw materials. In contrast with petroleum-derived fractions which consist primarily of hydrocarbons, lignocellulosic biomass is made up of carbohydrates and lignins. The former comprise hexoses and pentoses such as e.g. glucose, fructose, mannose, galactose, xylose and arabinose, while the lignins are polyphenolic materials composed of phenylpropane units (C-9 building blocks) (Figure 1).

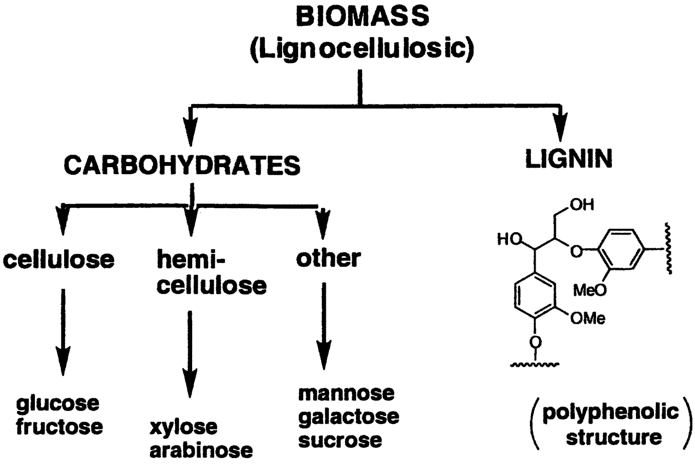
BIOMASS
(Lignocellulosic)
CARBOHYDRATES
LIGNIN
cellulose
hemi-cellulose
other
glucose
fructose
xylose
arabinose
mannose
galactose
sucrose
OH
HO
O
MeO
OMe
O
polyphenolic structure

Figure 1. Components of lignocellulosic biomass

The characteristically high degree of oxygenation causes biomass fractions and derivatives to be much more reactive than petrochemicals, and also precludes the use of many conventional catalyst systems and thermal processes. The higher polarity of the sugars is notoriously difficult to deal with in synthetic processes because one is often forced to take recourse to the use of hazardous solvents such as pyridine, or polar aprotic solvents such as acetonitrile, DMAc, DMF, DMSO, etc. to dissolve these polyhydroxylated substrates (*2*). The drawback then is that many efficient metal ion catalysts become too coordinated and less active towards sugars. It explains why free, i.e. unprotected, sugars are usually processed in aqueous solvent systems, and why most of the

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commercially interesting carbohydrate chemistry involves acid or base catalysis(*1,2*). More complex synthetic chemistry with carbohydrates can be made possible by selectively protecting the highly reactive hydroxy groups such that specific sites in the sugar molecule can be targeted. However, those protecting groups must be removed at a later stage, and decrease the overall efficiency and commercial attractiveness of the synthetic route. It is therefore not surprising that an important issue in modern carbohydrate chemistry is the search for synthetic pathways that completely bypass the need for such protection-deprotection steps (*2*).

With the advent of room-temperature ionic liquids (RTILs) in the arena of synthetic chemistry, it has become possible to expand on the existing series of traditional molecular solvents (*3,4,5,6*). RTILs are essentially non-aqueous salt-like materials that are liquid at or near room temperature, and the most common examples belong to the class of N,N'-disubstituted imidazolium salts (Figure 2).

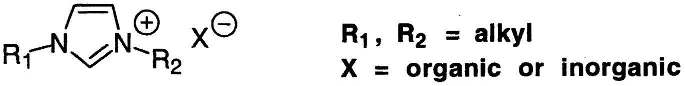

Figure 2. Depending on the choice of R and X groups, N,N'-imidazolium salts can become liquids at room temperature (RTIL).

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Depending on the substitution pattern of the imidazolium cation and the choice of anion, the RTIL can be made either hydrophobic or hydrophilic such that a wide range of substrates can be dissolved in these unique solvents. Other advantages of many RTILs are their negligible vapor pressure and often high thermal-, water- and air-stability, although these properties depend strongly on the choice of the anion. Imidazolium-based RTILs have been shown to be excellent media for a variety of catalytic reactions because the ionic medium is able to 'immobilize' transition metal ion catalysts. What is perhaps even more unique is that e. g. in the case of hydrophobic hexafluorophosphate salts, this happens without coordination of the metal catalyst.

Motivated by our mission to find new chemical methods to process biomass-derived sugars and lignins, we felt that it would be worthwhile to explore some chemistry with these challenging substrates in RTIL media (Table I), and to find out if new energy efficient and atom efficient processes could be developed. In this report, we will focus on our initial studies with carbohydrates since these are still the more interesting biomass components with respect to the production of chemicals and materials.

Sugars are notoriously prone to complex dehydration processes at higher temperatures, especially in the presence of acid or base catalysts (*1,2*).

Table I. Ionic Solvents used in this Study

R_1	R_2	X	Abbreviation	
Me	Bu	Cl	[bmim][Cl]	mp.65-69°C
Me	Bu	PF_6	[bmim][PF_6]	RTIL
Me	Bu	BF_4	[bmim][BF_4]	RTIL
Me	Oct	Cl	[moim][Cl]	RTIL

Note: [bmim][Cl] and [bmim][PF_6] were prepared according to ref. 7; [bmim][BF_4] was obtained following the procedure of ref. 8 (with isolation from aqueous phase at 5 °C).

Consequently, thermal isolation and purification steps (e.g. distillation) must be avoided. With that thought in mind, we envision a model reactor system that involves a simple vessel in which the feedstock material is allowed to react with a catalyst dissolved in a RTIL medium. Subsequent isolation of the products could be achieved through conventional solvent extraction with a solvent that is immiscible with the RTIL phase, or through simple decantation if there is phase separation. The ideal system would allow for recycling of the ionic catalyst solution to the reactor vessel, and this may be achieved by 'designing' the RTIL such that it acquires the appropriate solvent properties for a particular substrate.

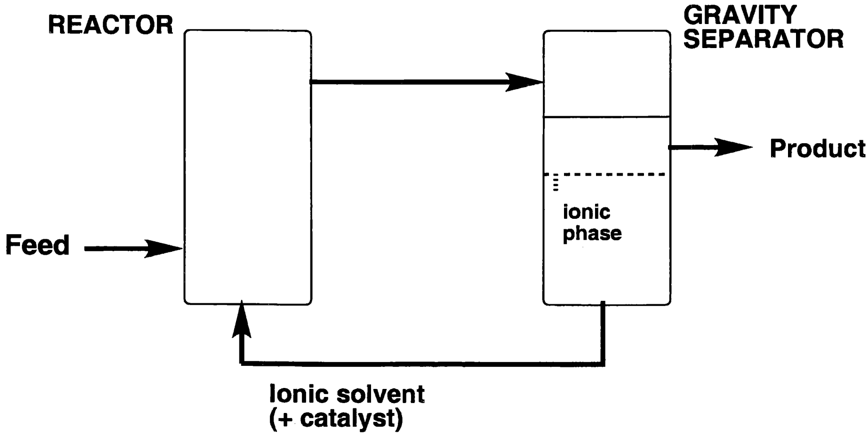

Figure 3. Conceptional design of a process reactor for biomass conversion in RTIL media with an immobilized catalyst.

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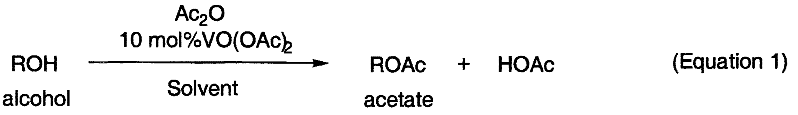
In order to test the concepts, we decided to try simple acylations of the hydroxy groups, since these are commonplace in sugar chemistry. Aside from catalytic methods that often involve toxic catalysts, reagents or solvents, the common procedures for effecting esterification of the hydroxy groups in sugars involve the use of stoichiometric quantities of strong base, such as e.g. sodium hydride or sodium hydroxide, in the presence of an acylating agent such as acyl halides or anhydrides in an organic solvent (9-*32*). An alternative approach would be to develop a solution of an 'immobilized' catalyst in an ionic liquid phase, and preferably a transition metal ion catalyst for which ligand(s) could be designed for optimal solubilities and turn-over numbers. Enzymatic acylation of simple alcohols has recently been demonstrated in ionic liquids, but the concept has not yet been applied to more complex polyols such as sugars (*33-37*).

During our search for viable catalysts, we became interested in a report that described the use of vanadyl(IV) acetate as an efficient Lewis acid catalyst for the acylation of alcohols with acetic anhydride in acetonitrile (Eq.1) (*38*).



$$\underset{\text{alcohol}}{\text{ROH}} \xrightarrow[\text{Solvent}]{\substack{\text{Ac}_2\text{O} \\ \text{10 mol\%VO(OAc)}_2}} \underset{\text{acetate}}{\text{ROAc}} + \text{HOAc} \qquad \text{(Equation 1)}$$

It can be obtained by simply heating vanadium pentoxide in acetic anhydride under reflux, is easy to handle and does not seem to exhibit any high sensitivity to air or moisture. The only drawback of using this particular catalytic system is that the acetylation results in the production of one mole equivalent of acetic acid that builds up during the process. However, for our purposes we had to first find out if this catalyst would be equally active in an ionic solvent medium, and secondly, we had to keep in mind that the hydroxy groups in a carbohydrate have different steric and chemical environments that could influence the rates of acetylation. Therefore we decided to start with partially protected monosaccharides that would allow us to evaluate the reactivity of primary *vs.* secondary OH-groups in the ring structure.

The acetonides shown in Figure 4 were treated with 0.1 mol equivalents of vanadyl(IV) acetate in the presence of 1.5 mol equivalents of acetic anhydride in 1-butyl-3-methylimidazolium hexafluorophosphate (or [bmim][PF_6]) as solvent. Monitoring of the catalytic process in the ionic medium by thin-layer chromatography (TLC) showed that any noticeable reaction occurred at higher temperature and longer reaction time compared to those carried out in acetonitrile. Even with these long reaction times, we had difficulties driving the reaction to completion. In addition, for lack of a better method, we had to extract the reaction product with an organic solvent, and this did not prove to be simple either. For instance, extraction with diethyl ether, ethyl acetate, methylene chloride, cyclohexane or toluene proved to be inefficient because part of the ionic liquid as well as small amounts of the vanadium catalyst were

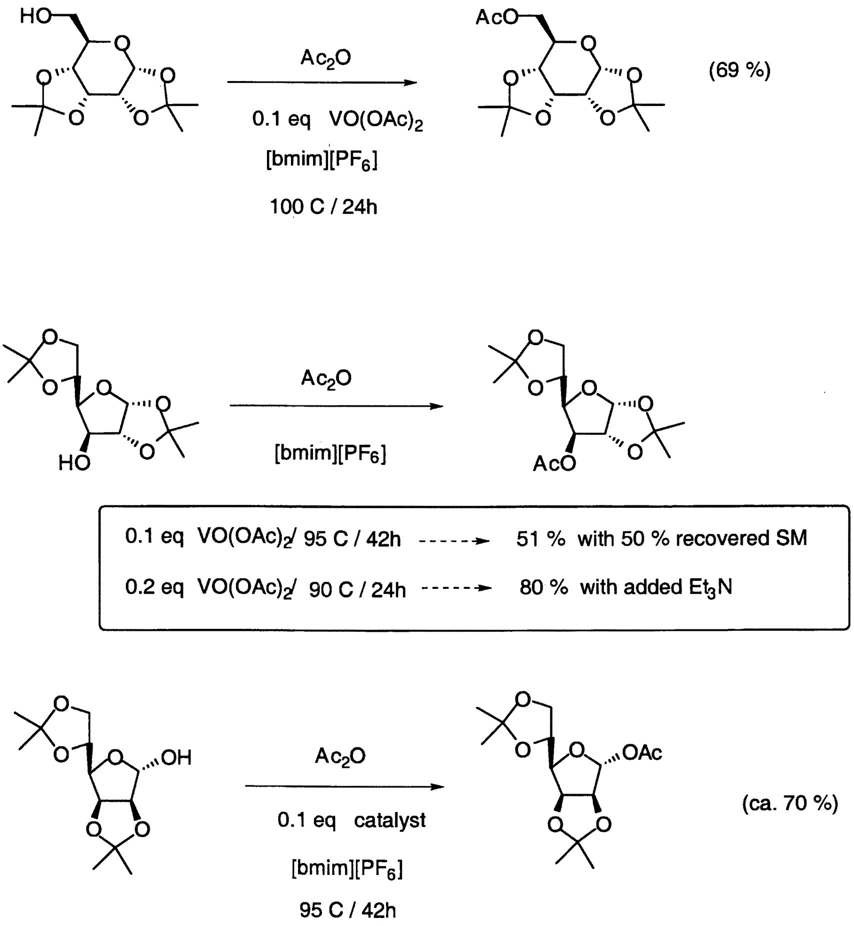

Ac2O
0.1 eq VO(OAc)2
[bmim][PF6]
100 C / 24h
(69 %)
Ac2O
[bmim][PF6]
0.1 eq VO(OAc)2/ 95 C / 42h -----> 51 % with 50 % recovered SM
0.2 eq VO(OAc)2/ 90 C / 24h -----> 80 % with added Et3N
Ac2O
0.1 eq catalyst
[bmim][PF6]
95 C / 42h
(ca. 70 %)

Figure 4. Acetylation of OH-groups under catalytic conditions in an RTIL.

soluble in these solvents also. These complications were minimized by using chloroform as an extraction solvent, which led to the yields shown in Figure 4.

As mentioned earlier, during these reactions a stoichiometric amount of acetic acid is formed as a by-product, and we suspected that this caused the

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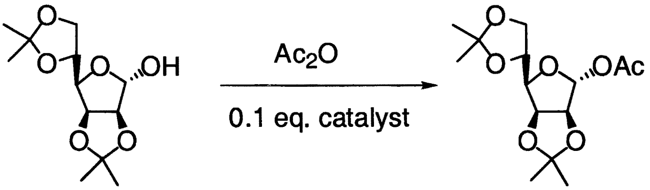
difficulties in driving the process to completion. This hypothesis found some support when we obtained a higher yield (from 51% to 80%) after adding a stoichiometric amount of triethylamine to one of the substrates. Without this weak base, about half of the starting material remained unreacted. Attempts to improve the yield with another V(IV) catalyst, i. e. VO(salen), did not improve the yields or decrease the required reaction temperature, but interestingly we obtained a quantitative yield of acetylation at an anomeric center when [bmim][Cl] was used as a reaction medium (Figure 5).



Catalyst	Ionic solvent	T (°C)	t (h)	Yield (%)
$VO(OAc)_2$	$[bmim][PF_6]$	95	9	66
VO(salen)	$[bmim][PF_6]$	95	48	66
VO(salen)	[bmim][Cl]	90	3	100

VO(salen) =

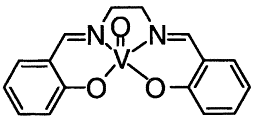
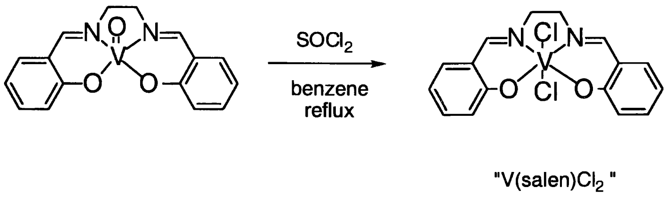


Figure 5. Improvement of the yield of acetylation by changing the ionic solvent.

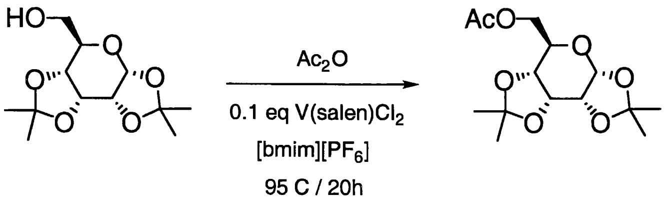
Note that the reaction time was also lowered to only 3 h. This ionic medium is solid at room temperature (mp 65-69°C) and is completely water-soluble. The work-up therefore consisted of dissolving the reaction mixture in water, followed by extraction of the product from the homogeneous aqueous phase with methyl isobutyl ketone. Clearly, this did not allow for a straightforward recycling of the catalyst.

Due to the partial solubility of the catalyst in a variety of organic extraction solvents, we then made a slight modification to the VO(salen) catalyst, by treating it with thionyl chloride as shown in Equation 2 (*39*). This generates a blue dichlorovanadium(IV) complex, i. e. $V(salen)Cl_2$, which belongs to a class of vanadium compounds that, to the best of our knowledge has not yet received any attention in the literature as a potentially useful Lewis acid catalyst for synthetic chemistry. Nevertheless, a variety of dichlorovanadium(IV) have been



(Equation 2)

described in the literature (*40*). Our hope was that this halogenated complex would be a stronger electrophile than the parent VO(salen), resulting in higher rates of acetylation. Unfortunately, this did not materialize, but we did notice that the characteristic blue color of this catalyst remained immobilized in the ionic phase (Equation 3). We also found that isopropanol could be used instead of chloroform to extract the product without removing this catalyst from the ionic phase (*41*). Indeed, in a first run, we obtained a 60% yield of the acetylated substrate, and because of the improved immobilization of the catalyst, we were able to recycle the active, blue-colored catalyst phase a second time to obtain 71% yield. However, the blue color of the catalyst faded after this second step and we suspect that it underwent slow hydrolysis of the V-Cl bonds with traces of moisture. We have not yet determined the lifetime of this catalyst under more stringent anhydrous conditions, nor have we finished our exploration of different ligands on the vanadyl(IV) complexes.



(Equation 3)

While the reactivity of the catalyst is an important factor, the choice of anion in the RTIL turned out to be crucial for obtaining good yields. As shown in Figure 6 , use of the chloride salt is by far the most appropriate ionic solvent since it allows the reaction to go to completion. In the case of both the hydrophobic PF_6 salt and the much more hydrophilic BF_4 salt, we recovered substantial amounts of starting material when the reactions were carried out within a similar time period (50% and 26% respectively, within 5-6 h of reaction time). This indicates that the catalyst does not have the same level of activity in these different media. In the absence of the vanadium catalyst, the yield of the sugar acetate was very low, even after almost two days of reaction at high

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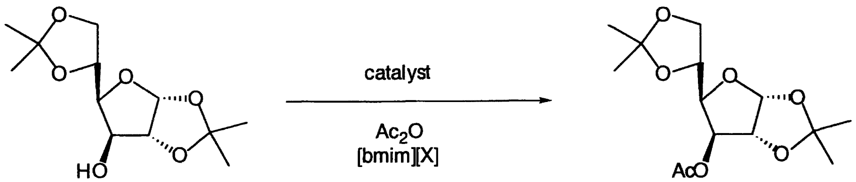
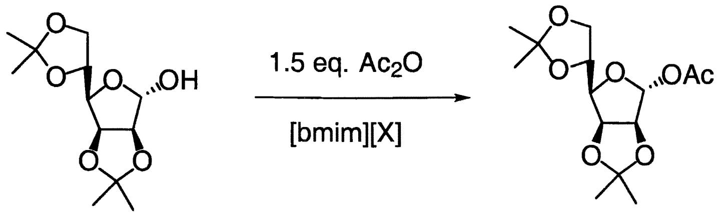


X	Ac_2O (equiv)	T (°C)	t (h)	Catalyst	Yield (%)
Cl	1.5	90	5	$VO(OAc)_2$	91
Cl	3.0	70	24	-	98
BF_4	1.5	80	6	$VO(OAc)_2$	39 (26 SM)
PF_6	1.5	90	6	$VO(OAc)_2$	50 (50 SM)
"	3.0	90	48	-	5 (75 SM)
"	"	95	42	$VO(OAc)_2$	51 (50 SM)
"	"	90	24	$VO(OAc)_2$ / Et_3N	80

Figure 6. Influence of RTIL anion on product yields, with and without catalyst. The hydrophobic RTIL requires the use of added vanadium catalyst.

temperature. Again, the yield improved dramatically when a mole equivalent of triethylamine was added. The most surprising observation, however, was that a reaction in [bmim][Cl] without catalyst led to a near quantitative yield of product. This suggests that the use of any transition metal catalyst may be bypassed by using chloride salts as ionic liquids. We found a similar reactivity with an acetonide that has an unprotected anomeric OH-group (Figure 7). The resulting esterification reaction proceeded with retention of the stereochemical orientation of the anomeric group, which suggests that there is no significant solvolysis taking place in the highly ionic medium. Although we did not find any signs of racemization for this particular case, there is certainly room for exploration in this area with a variety of carbohydrates to figure out how the anomeric groups may be susceptible to solvolytic effects in ionic media.

Using the data that we obtained with the partially protected sugars, we wanted to know if peracetylation, i. e. acetylation of all OH-groups in an unprotected sugar molecule, could be achieved in [bmim][Cl] as reaction medium. Table II shows a few examples of free sugars that were peracetylated efficiently in molten [bmim][Cl], and no additional catalyst was needed to effect this transformation. A lower yield was obtained in the case of the D-xylose, where we observed a by-product that appears to be the acetylated form of the open chain structure. This brings up an interesting issue that will also require more extensive investigations, i. e. what is the equilibrium of open *vs.* closed chain isomers of different sugars in the ionic media? To the best of our



X	T (°C)	T (h)	Yield (%)
Cl	85	7	99
PF_6	85	16	2

Figure 7. Acetylation of anomeric OH-group in the absence of catalyst.

knowledge, there are no commercial sources yet for deuterated imidazolium salts that could be used as NMR solvents. We are aware of only one recent report that deals with the preparation of deuterated RTILs, and obviously these compounds will be needed for advancing sugar chemistry in ionic liquids. The chemistry that takes place in the [bmim][Cl] media is not clear although we believe that the chloride anion may actually be a reaction partner in the process. The latter could react with the acetic anhydride to generate small amounts of acetyl chloride which under equilibrium conditions becomes the active acetylating agent for the OH-group. We are currently investigating the mechanism of this reaction, as well as its scope and limitations for mono- and polysaccharides.

Table II. Peracetylation of unprotected sugars in [bmim][Cl]

Sugar	*Ac_2O (equiv)*	*T (°C)*	*t (h)*	*Yield (%) of peracetylation*
D- glucose	10	65	6	99
D-xylose	8	65	8	72
L-arabinose	8	65	5	100

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Although we are still at the preliminary stage, we have found that 0.25 M solutions of several free sugars can be prepared at room temperature in 1-methyl-3-octylimidazolium chloride or [moim][Cl], that, unlike [bmim][Cl], is a liquid at room temperature. Not surprisingly, one has to apply a considerable anmount of heat to dissolve the free sugars in the hydrophobic [bmim][PF_6].

Table III. Temperatures of dissolution of free sugars

Sugar	*mp (°C)*	*Dissolution in [bmim][PF_6]*	*Dissolution in [moim][Cl]*
D-mannose	133-140	103-5	RT
D-glucose	153-6	100-2	RT
D-xylose	156-8	95-7	RT
D-arabinose	162-4	110-2	RT

Note: the sugars were used as received and were not predried.

Even though clear solutions were obtained at those higher temperatures, we noticed the beginning of discoloration of the solutions, which could be attributed to thermal decomposition of the sugars. Here also, we need to obtain more data for many sugars in a wider variety of RTILs with different polarities. The issue that needs to be addressed is how free mono- and polysaccharides behave when they have been predried compared to samples that still contain their crystal water.

Conclusions

We have demonstrated that ionic liquids can be used as alternative solvent media for the esterification of sugars and sugar derivatives. The important lesson that we learned in this preliminary investigation is that hydrophobic ionic liquids such as [bmim][PF_6] do not dissolve free sugars very well, and that they will support acetylation of the OH-groups only in the presence of a catalyst. On the other hand, the hydrophilic ionic media such as [bmim][Cl] obviate the need for any dissolved catalyst, but these salts appear to be participants in the reaction process. Further work is needed to gain a better understanding of the mechanism of this reaction. As mentioned before, the scope and limitations of reactions in ionic media such as [bmim][Cl] and [moim][Cl] need to be investigated, and could provide new methodology for peracylating not only refined mono- and polysaccharides to make high(er)-value products, but maybe also whole biomass samples. Another focus would be to find acylating agents other than the acid anhydrides that result in the formation of a molar equivalent of carboxylic acid as a by-product.

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Earlier in this Chapter, we pointed out that the non-coordinative character of the hydrophobic RTILs such as [bmim][PF_6] offers unique possibilities with respect to catalysis with transition metal catalysts. Our finding that free sugars are more soluble in the hydrophilic and highly coordinating chloride salts shows that much more work is needed to find an appropriate (non-coordinating) ionic liquid that can support catalytic processes for converting sugars. Nonetheless, from our work with the chloride salt it is clear that possible reactivity of the solvent itself may be a useful tool to effect certain chemical transformations.

Probably one of the most emphasized areas in carbohydrate chemistry is the stereocontrol in reactions at the anomeric center since it lies at the basis of many important glycosylation reactions in the synthesis of oligo- and polysaccharides. Even though we have not yet investigated any reactions wherein the anomeric C-O bond is affected, it is not inconceivable that an ionic medium may influence solvolytic processes in ways that are not possible in traditional molecular solvents. Therefore, we consider detailed solvolysis studies of sugars in ionic liquids to be an important and necessary area of future work. Here also, the availability of deuterated RTILs will be important because, as mentioned earlier, the equilibrium concentrations of the open *vs.* closed chain conformation of the sugars in an ionic medium must be known for the reactions with certain partially protected or completely unprotected carbohydrates.

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Chapter 29

Biphasic Hydroformylation Using Ionic Liquids

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Two different approaches for the biphasic hydroformylation of 1-octene using ionic liquids are presented in detail. a) the Pt-catalyzed hydroformylation in chlorostannate ionic liquids; b) the Rh-catalyzed hydroformylation in hexafluorophosphate systems. For the latter case, the use of special ionic ligands is required to achieve full catalyst immobilization in the ionic liquid. The synthesis and application of successful cationic ligands systems is described.

Why Use Ionic Liquids As Solvents For Biphasic Hydroformylation?

Biphasic catalysis is a well-established method for effective catalyst separation and recycling. In the case of Rh-catalyzed hydroformylation reactions this principle is technically realized in the Ruhrchemie-Rhône-Poulenc-process, where water is used as catalyst phase (*1*, *2*, *3*). Unfortunately, this process is limited to C_2-C_5-olefins due to the low water solubility of higher olefins. Nevertheless, the hydroformylation of e.g. 1-octene is of technical interest for the synthesis of linear nonanal. To produce the latter in high selectivity, it is

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necessary to achieve a highly regioselective hydroformylation. This can be realized by application of special ligand systems. Obviously, the additional costs for these ligands make it even more economically attractive to develop methods for an efficient catalyst separation and recycling.

Recently, a new approach has been adopted for biphasic catalysis, involving the use of catalyst solvents known as ionic liquids, which are simply salt mixtures of low melting points (< 100°C). Ionic liquids form biphasic systems with many organic liquids such as e.g. α-olefines. Moreover, their non-volatile character allows distillative product separation from the catalyst without the formation of azeotrops and without solvent contamination in the product (*4*, *5*, *6*).

Depending on the coordinative properties of its anion, the role of an ionic liquid in homogeneous catalysis can be regarded as either "innocent" solvent or solvent/cocatalyst. Ionic liquids with tetrafluoroborate or hexafluorophosphate ions, for example, have to be considered as neutral and inert solvents in most hydroformylation reactions (if carbene formation from the imidazolium cation is avoided). In these cases the function of the ionic liquid is solely to provide a polar, weakly coordinating medium for the transition metal catalyst that additionally offers special solubility for feedstock and products. However, ionic liquids formed by the reaction of a halide with a Lewis acid (e.g. chloroaluminate or chlorostannate melts) generally act as well as a cocatalyst. The reason for this is the Lewis acidity or basicity which is always present (at least latent), and which results in strong interactions with the catalyst complex. In many cases, the Lewis-acidity of an ionic liquid is used to convert the neutral catalyst precursor into the corresponding cationic active form.

In biphasic hydroformylation reactions both types of ionic liquids have been successfully applied. While in the Pt-catalyzed hydroformylation slightly acidic chlorostannate ionic liquids are known to activate the precursor complex in a Lewis-acid/base reaction (*7*), hydroformylation with Rh-complexes has been carried out in "neutral" ionic liquids such as e.g. hexafluorophosphate systems (*8*, *9*, *10*). The following chapters intend to give a summary of recent progress in both areas.

For several reasons only those examples will be discussed where 1-octene has been used as the substrate: (a) in order to allow a comparative discussion of the different approaches; (b) since all tested ionic liquids form biphasic reaction systems with 1-octene; (c) due to the technical importance of the 1-octene hydroformylation; 1-nonanal is an important intermediate for the synthesis of plasticizer alcohols; (d) since 1-octene hydroformylation with aqueous catalyst solutions is not successful; 1-octene solubility in water is only in the range of

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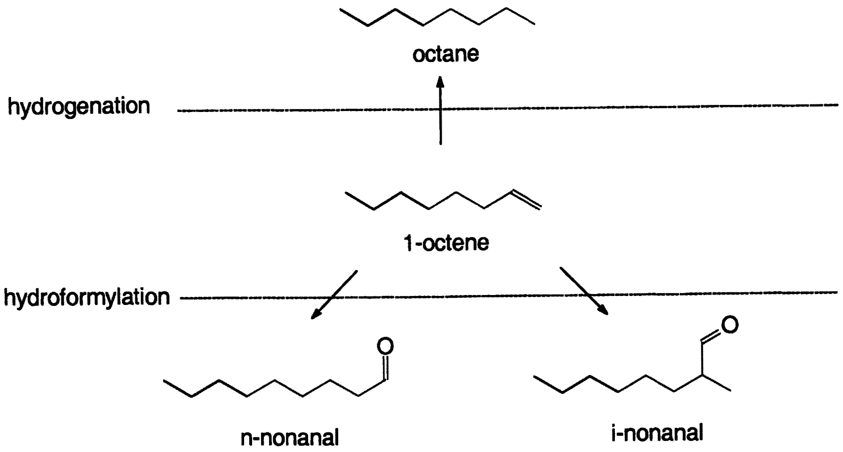

Figure 1: Hydroformylation of 1-octene

0.0001 mol% at 25°C (3) while 1-octene solubility in e.g. [BMIM] [PF_6] is about 2.5 mol% at 25°C (*11*). In figure 1, general aspects of the 1-octene hydroformylation are summarized.

Hydroformylation Of 1-Octene In Chlorostannate Ionic Liquids Using Pt-Catalysts

Platinum(II) complexes with phosphine ligands promoted by $SnCl_2$ are known as hydroformylation catalysts since 1976 (*12*). Systems with monodentate phosphines have been investigated in the hydroformylation of terminal and internal olefins (*13*, *14*, *15*, *16*, *17*, *18*, *19*, *20*). Pt/Sn catalysts with diphosphines have been successfully applied to the asymmetric hydroformylation (*21*, *22*, *23*, *24*, *25*) and to the highly regioselective hydroformylation of internal, functionalized olefins (*26*).

The Platinum-catalysed hydroformylation of ethylene in a tetraethylammoniumchlorostannate molten salt (melting point: 78°C) was described by Parshall as early as 1972 (*27*). This publication showed for the first time the potential of a chlorostannate ionic liquid as reaction medium for a homogeneous Platinium-catalyst. However, the relatively high melting point of the chlorostannate salt used by Parshall caused some restrictions for reaction parameters and processing conditions. The experiments were carried out under

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extreme conditions (syngas pressure of 400 bars). Finally, in Parshall's publication the activity of the catalyst has not been determined quantitatively. Therefore it is not possible to compare the catalyst's performance in the chlorostannate melt with the results in conventional organic solvents.

Recently, room temperature liquid chlorostannate ionic liquids were used to investigate the potential of Pt-complexes in the hydroformylation of 1-octene (*7*). Those low melting chlorostannate salts have been described by Ling et al. as solvents for electrodeposition of tin and other electrochemical applications (*28*).

Chlorostannate ionic liquids are easily prepared by mixing imidazolium or pyridinium chloride salts with the appropriate amount of $SnCl_2$ (*7*). To form the ionic catalyst solution, e. g. $(PPh_3)_2PtCl_2$ is added to the chlorostannate ionic liquids. A change in color from yellow to red is observed. Probably, this is attributed to the abstraction of chloride atoms from the Pt-complex by the acidic $Sn_2Cl_5^-$-species of the ionic liquid (as shown in figure 2). This assumption can be supported by recording the Lewis-acidity of the chlorostannate ionic liquid before and after the addition of $(PPh_3)_2PtCl_2$ by ^{119}Sn-NMR (*7*). The results of this investigation corresponded very well to an acid-base reaction of both chloride atoms of the Platinum-complex with the acidic ionic liquid.

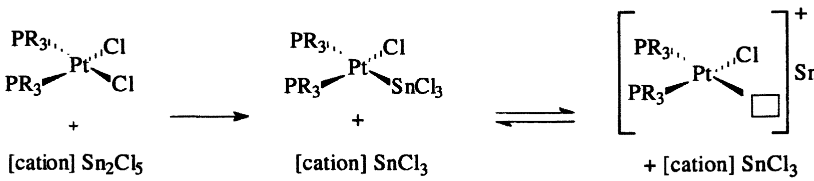

Figure 2: Activation of $(PPh_3)_2PtCl_2$ in an acidic chlorostannate ionic liquid (proposed mechanism)

Table 1 shows the results obtained with $(PPh_3)_2PtCl_2$ in two different chlorostannate ionic liquids in comparison to the experiment in CH_2Cl_2 under identical conditions (*7*).

While the reaction is found to be monophasic in CH_2Cl_2, a biphasic reaction takes place with each of the chlorostannate ionic liquids. Moreover, no leaching of the Pt-catalyst is detected, which can be interpreted as another strong hint for the postulated ionic structure of the active Pt-catalyst. The ionic catalyst solution can be recovered after catalysis by simple phase separation.

The hydroformylation in CH_2Cl_2 shows (in good accordance to the known literature (*26*)) reasonable activity with very high selectivity to the linear nonanal

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Table 1: Hydroformylation of 1-octene using different solvents

	Solvent	*Conversion [%]*	*TOF* $[h^{-1}]$	*S(n-nonanal)*$^{a)}$ *[%]*	*S(octane)*$^{b)}$ *[%]*
a	[4-MBP] Cl/$SnCl_2$	19.7	103	96.0	29.4
b	[BMIM] Cl/$SnCl_2$	22.3	126	95.0	41.7
c	CH_2Cl_2	25.7	140	98.3	9.4

Conditions: 0.02 mmol $PtCl_2(PPh_3)_2$, 0.1 mmol PPh_3, 20 mmol 1-octene, 5 ml solvent, $p(CO/H_2)$= 90 bar, T= 120 °C, t= 2h; Entries a,b: X_{SnCl2}= 0.51. a) The selectivity for n-nonanal was calculated in the following way: [S(n-nonanal)]= amount of n-nonanal/amount of all hydroformylation products. b) The selectivity for octane was calculated in the following way: [S(octane)]= amount of octane/amount of all products.

(entry c in table 1). The undesired hydrogenation of 1-octene to octane is moderate in CH_2Cl_2. In contrast, in both chlorostannate ionic liquids slightly lower rate, still very high n/iso-selectivity, but higher hydrogenation activity (entries a and b in table 1) is obtained. Interestingly, the undesired hydrogenation activity depends significantly on the cation of the ionic liquid (41.7% hydrogenated product with 1-*n*-butyl-3-methylimidazolium[BMIM] cation versus 29.4% with 1-*n*-butyl-4-methylpyridinium[4-MBP] cation).

More detailed studies to identify the best reaction conditions revealed that in the chlorostannate ionic liquids the highest ratio of hydroformylation to hydrogenation is found at high syngas pressure and low temperature. At 80 °C and 90 bar CO/H_2-pressure more than 90 % of all product are n-nonanal and iso-nonanal, the ratio between these two hydroformylation products being as high as 98.6:1.4 (n:i = 72.4) (7).

In conclusion, these results show that room temperature liquid chlorostannate ionic liquids are versatile solvents for the regioselective hydroformylation of 1-octene. Moreover, the experiments reveal some unique properties of chlorostannate ionic liquids. In contrast to other known ionic liquids, the chlorostannate system combine a certain Lewis-acidity with high compatibility to functional groups. The first led in the hydroformylation of 1-octene to the activation of $(PPh_3)_2PtCl_2$ by a Lewis-acid-base reaction with the acidic ionic liquid medium. The high compatibility to functional groups is demonstrated by the catalytic reaction in presence of CO and hydroformylation products.

Hydroformylation Of 1-Octene With Rh-Catalysts In Ionic Liquids

Already in 1995, Chauvin et al. described the biphasic hydroformylation of 1-pentene with [Rh(CO)$_2$acac]/triarylphosphine in *e.g.* [BMIM] [PF$_6$] (*8*, *29*). However, with none of the tested ligands it was possible to combine high activity, complete retention of the catalyst in the ionic liquid and high selectivity for the desired linear hydroformylation product. The use of PPh$_3$ resulted in significant leaching of the Rh-catalyst out of the ionic liquid layer. This could be suppressed by the application of sulfonated triaryl phosphine ligands, but a major decrease in catalytic activity was found with these ligands. All ligands used in Chauvin's work showed poor selectivity to the desired linear hydroformylation product (*n/iso*-ratio between 2 and 4). Obviously, the Rh-catalyzed, biphasic hydroformylation of higher olefins in ionic liquids requires the use of ligand systems that are specifically designed for this application.

Cationic phosphine ligands designed for the use in ionic liquids

Cobaltoceniumdiphosphine ligands

A first ligand system designed for the use in ionic liquids was described in 2000 by Salzer et al. (*9*). These authors used successfully cationic ligands with cobaltocenium backbone for the biphasic, Rh-catalyzed hydroformylation of 1-octene. 1,1'-Bis(diphenylphosphino)cobaltocenium hexafluorophosphate (cdpp) proved to be an especially promissing ligand. The compound can be synthesized according to figure 3 by mild oxidation of 1,1'-bis(diphenylphosphino)cobaltocene with C$_2$Cl$_6$ and anion exchange with [NH$_4$][PF$_6$] in acetone. (for detailed ligand synthesis see (*9*)).

The catalytic systems are prepared *in situ* by mixing [Rh(CO)$_2$acac] with the ligand in [BMIM] [PF$_6$] at room temperature. [BMIM] [PF$_6$] is prepared by reacting the chloride salt (see literature (*30*) for detailed synthesis) with HPF$_6$ after a method described by Fuller and Carlin (*31*) or purchased from Solvent Innovation GmbH, Cologne (*32*).

The results obtained in the biphasic hydroformylation of 1-octene are presented in table 2. In order to evaluate the properties of the ionic diphosphine ligand with cobaltocenium backbone, the results with ligand cdpp are compared with those obtained with PPh$_3$, two common neutral bidentate ligands and with NaTPPTS as standard anionic ligand (*9*).

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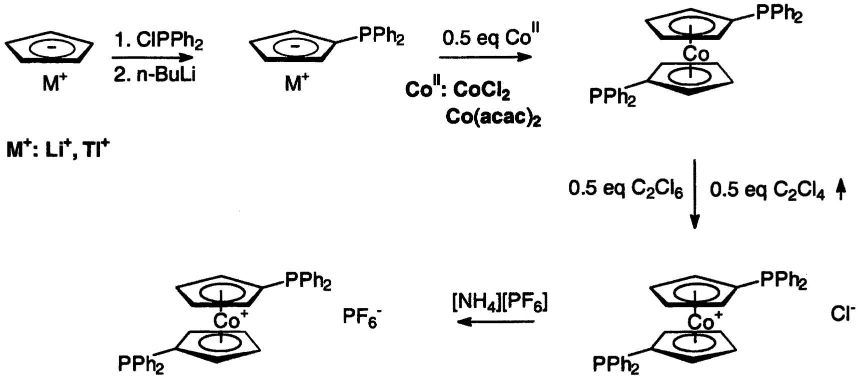

Figure 3: Synthesis of 1,1'-Bis(diphenylphosphino)cobaltocenium hexafluorophosphate

Table 2: Comparison of different phosphine ligands in the Rh-catalysed hydroformylation of 1-octene in [BMIM][PF_6]

	Ligand	*TOF / h^{-1}*	*n/iso*	*S (n-Ald)[a] / %*
a	PPh_3	426	2.6	72
b	TPPTS	98	2.6	72
c	dppe	35	3.0	75
d	dppf	828	3.8	79
e	cdpp	810	16.2	94

Conditions: Ligand/Rh: 2, CO/H_2=1:1, t= 1h, T= 100°C, p= 10 bar, 1-octene/Rh= 1000, 5 mL [BMIM] [PF_6]; dppe: bis(diphenylphosphinoethan); dppf: 1,1'-bis(diphenylphosphino)ferrocene; [a] S (n-Ald)= Selectivity to *n*-nonanal in the product.

It is noteworthy that only with cdpp a clear enhancement of the selectivity to the linear hydroformylation product is observed (Table 2, entry e). With all other ligands, the *n/iso*-ratios are in the range between 2 and 4. While this is in good accordance to known results in the case of PPh_3 (Table 2, entry a) and dppe (Table 2, entry c) (in comparison to the monophasic hydroformylation (*33*)) and also in good accordance to reported results in the case of NaTPPTS (in comparison to the biphasic hydroformylation of 1-pentene in [BMIM] [PF_6] (*8*)), it is more remarkable for the bidentate metallocene ligand dppf.

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In this respect, a direct comparison of the results obtained with the isoelectronic and isostructural metallocene ligands dppf and cdpp is of particular interest (comparison of entries d and e in Table 2). Taking into account the high structural similarity of both ligands, their different influence on the reaction's selectivity has to be attributed to electronic reasons. The electron density at the phosphorus atoms is significantly lower in the case of ligand cdpp due to the electron-withdrawing effect of the formal cobalt(III) central atom in the ligand. This interpretation is supported by former work from Casey et al. (*34*) and Duwell et al. (*35*). These groups described positive effects of ligands with electron-poor phosphorous atoms in selective hydroformylation reactions which they attribute to their ability to allow back-bonding from the catalytically active metal atom.

It has to be pointed out that only with the phosphinocobaltocenium ligand cdpp the reaction takes place exclusively in the ionic liquid phase (clear and colorless organic layer). With all other ligands, a significant leaching of the catalyst into the organic layer is observed (deep yellow color of the organic phase). In the latter case, the catalyst is active in both phases, which makes a clear interpretation of solvent effects on the reactivity difficult.

In the case of cdpp being the ligand an easy catalyst separation by decantation was possible. Moreover, it was found that the recovered ionic catalyst solution could be reused at least one more time with the same activity and selectivity as in the original run (*9*).

Guanidinium modified triphenylphosphine

Cationic phosphine ligands containing guanidiniumphenyl moities have been originally developed to make use of their pronounced solubility in water (*36*, *37*). They were shown to form active catalytic systems in Pd mediated C-C coupling reactions between aryl iodides and alkynes (*36, 38*) (Castro-Stephens-Sonogashira reaction) and Rh catalysed hydroformylation of olefins in aqueous two-phase systems (*39*).

Recently, it was found that the modification of neutral phophine ligands with cationic phenylguanidinium groups represents a very powerful tool to immobilise Rh-complexes in ionic liquids such as e. g. [BMIM] [PF_6](*10*). The guanidinium modified triphenylphosphine ligand was prepared according to figure 4 by anion exchange with [NH_4][PF_6] in aqueous solution from the corresponding iodide salt. The latter can be prepared as previously described by Stelzer et al. (*37*).

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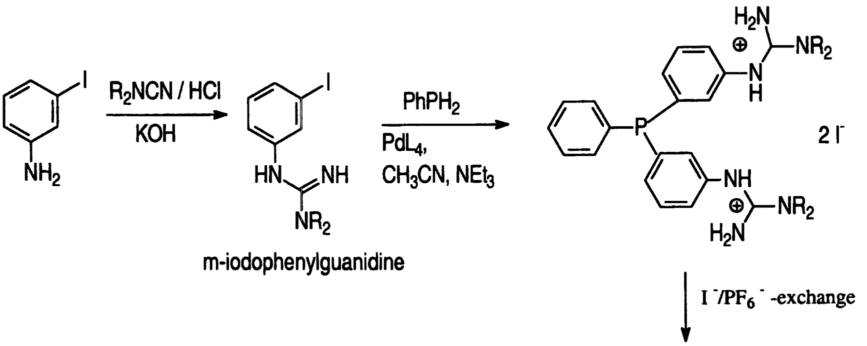

Figure 4: Synthesis of a guanidinium modified triphenylphosphine ligand

The comparison of triphenylphosphine and the guanidinium modified triphenylphosphine ligand in the biphasic hydroformylation reveals a number of important differences. In the reaction with PPh_3 good catalytic activity is observed but obviously a significant part of the hydroformylation reaction takes place in the organic layer. Due to severe leaching, 53% of the used Rh is found in the organic layer after reaction after the first catalytic run (according to ICP analysis). The recycled ionic catalyst solution possesses only 15% of its original activity in the third recycling run.

In contrast, with the guanidinium modified triphenylphosphine the hydroformylation reaction takes places uniquely in the ionic liquid layer. In the first catalytic run the hydroformylation activity is found to be somewhat lower than in case of PPh_3 (probably due to some mass transfer limitation of oct-1-ene into the ionic liquid). However, due to the excellent immobilisation of the Rh-catalyst with this ligand (leaching is $< 0.07\%$ per run according to ICP analysis (detection limit)), the catalytic activity does not drop over the first ten recycling runs. Already after five recycling runs, the overall catalytic activity obtained with the guanidinium modified ligand is higher than the one that is possible with the simple PPh_3 ligand. With both ligands the *n/iso*-ratio of the hydroformylation products is in the expected range of 1.7-2.8 (10).

Guanidinium modified diphosphine ligands with a xanthene backbone

Further development aimed to adopt this immobilisation concept to a ligand structure that promises better regioselectivity in the hydroformylation reaction. It is well-known that diphosphine ligands with large natural P-metal-P bite angles form highly regioselective hydroformylation catalysts (*40*). Here, xanthene type ligands (P-metal-P~ 110 °) developed by van Leeuven's group proved to be especially suitable allowing e. g. an overall selectivity of 98% towards the desired linear aldeyd in 1-octene hydroformylation (*41*, *42*).

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While unmodified xanthene ligands (see figure 5) show in a biphasic mixture 1-octene/[BMIM] [PF_6] even at room temperature highly preferential solubility in the organic phase, the application of guanidinium-modified xanthene ligands resulted in excellent immobilisation of the Rh-catalyst in the ionic liquid.

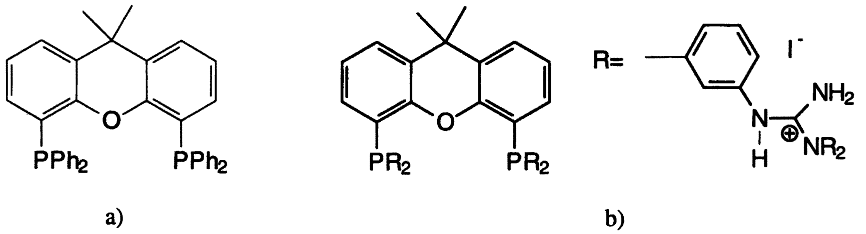

Figure 5: Unmodified (a) and guanidinium-modified xanthene ligand (b) as used in the biphasic, Rh-catalysed hydroformylation of 1-octene

The guanidinium modified ligand was synthesised in four steps according to figure 6.

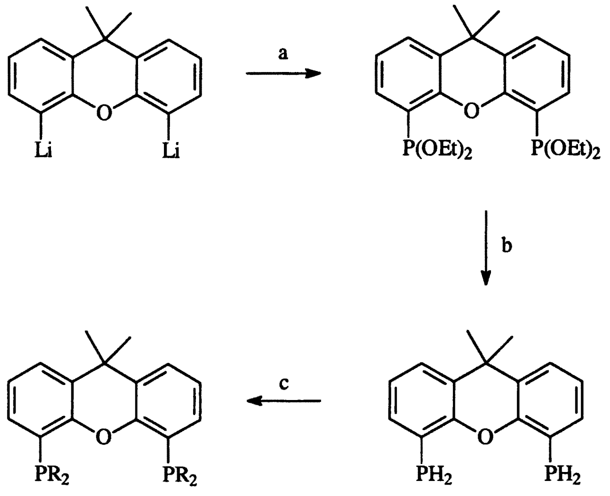

*Figure 6: Synthesis of a guanidinium modified xanthene ligand a) diethylchlorophosphite; b) $LiAlH_4$/chlorotrimethylsilane; c) 4 eq. 3-iodophenylguanidine, 2 mol% Pd_2dba_3 * $CHCl_3$, 80 °C, 24h in DMF.*

After dilithiation of the xanthene moiety, reaction with diethylchlorophosphite (figure 6, step a) and reduction with $LiAlH_4$ (figure 6, step b), the diprimarily xanthenediphosphine was obtained according to van Leeuwen et al. (*43*). The reaction of the diprimarily phosphine with iodophenylguanidine proceeded in a Pd(0)-catalysed coupling reaction (figure 6, step c). After 24h reaction time at 80 °C in DMF, the diprimary phosphine was completely converted to the guanidinium modified xanthene ligand.

The ligand was tested in ten consecutive hydroformylation runs. After each run the organic layer was decanted off (under normal atmosphere) and the ionic catalyst layer remained in the autoclave for the next run. The results are presented in figure 7. It is noteworthy that the catalytic activity increases during the first runs to obtain a stable level only after the forth recycling run. This behaviour is attributed not only to a certain catalyst preforming time but as well to impurities of iodoaromate in the used ligand. Probably, these are slowly washed out of the catalyst layer during the first catalytic runs.

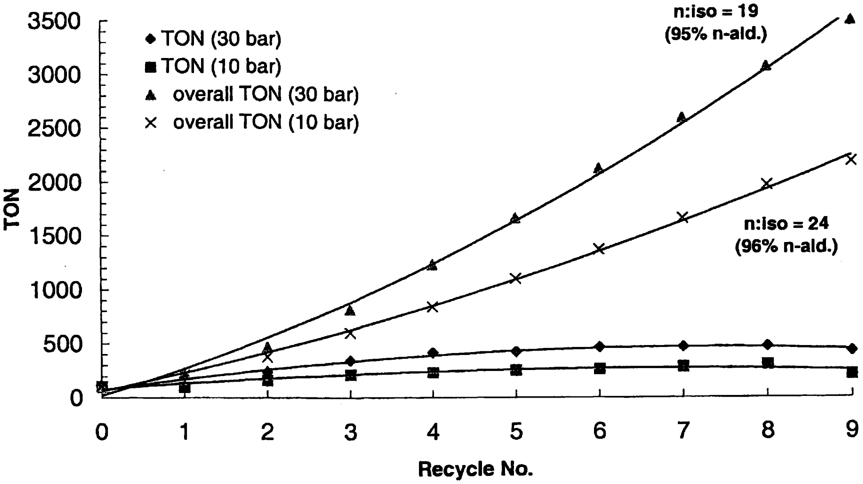

Figure 7: Recycling experiments – Rh-catalysed, biphasic 1-octene hydroformylation in [BMIM] [PF_6] using a guanidinium modified diphosphine ligand with xanthene backbone

After ten consecutive runs the overall turnover number reaches up to 3500 mol 1-octene converted per mol Rh-catalyst. In agreement with these recycling experiments, no Rh could be detected in the product layer by AAS and ICP indicating a leaching of less then 0.07 %. In all experiments very good selectivities for the linear aldeyde were obtained thus proving that the attachment

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of the guanidinium moiety to the xanthene backbone does not influence its known positive effect on the regioselectivity of the reaction.

In conclusion, these results show that the modification of known phosphine ligands with guanidinium groups represent a simple and very efficient method to fully immobilise transition metal complexes in hexafluorophosphate ionic liquids. Hereby, the electronic properties of the phosphine are not changed significantly. This immobilisation method may therefore be of interest not only for hydroformylation but also for many other catalytic reactions in ionic liquids.

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Conclusion and Outlook

Two different approaches to carry out biphasic hydroformylation of 1-octene with ionic liquids have been described. a) Pt-catalyzed hydroformylation in slightly acidic chlorostannate ionic liquids where the ionic liquid acts as solvent and cocatalyst. b) Rh-catalyzed hydroformylation in hexafluorophosphate ionic liquids where the ionic liquid acts as "innocent" solvent with special solubility properties.

The Pt-catalyzed hydroformylation in chlorostannate melts reveals some interesting properties of the chlorostannate ionic liquids but suffers from moderate rates and relatively high hydrogenation activity. However, the immobilization of the active catalyst in the ionic liquid is excellent and very high regioselectivity can be obtained.

The Rh-catalyzed hydroformylation in hexafluorophosphate melts requires the use of especially designed ionic ligand systems to immobilize the neutral Rh-complex in the ionic liquid. Cationic phosphine and diphosphine systems proved to be successful. Guanidinium modified diphosphine ligands with xanthene backbone and cobaltoceniumdiphophine systems enable a highly selective hydroformylation of 1-octene and very good catalyst immobilization in the ionic liquid. A clear enhancement of the overall catalytic activity could be achieved by repetitive use of the ionic catalyst solution.

Acknowledgements

We would like to take the opportunity to thank Prof. Salzer, Prof. Stelzer, Dr. Brasse and Dr. Machnitzki for an excellent collaboration in the field of hydroformylation chemistry with ionic liquids over the last years. Moreover, we wish to thank Prof. Willi Keim for his continuous support and his great interest in our work. Financial support by the European Community (under the BRITE/EuRam-project BE96-3745) for some of the here cited work is gratefully acknowledged.

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Chapter 30

Chymotrypsin-Catalyzed Transesterification in Ionic Liquids and Ionic Liquid/Supercritical Carbon Dioxide

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The potential utility and versatility of biotransformations in ionic liquids and ionic liquids mixed with supercritical carbon dioxide is demonstrated using a model enzyme reaction. The characteristics of enzyme activity in the ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate and 1-octyl-3-methylimidazolium hexafluorophosphate are consistent with those observed in conventional organic solvents. The presence of supercritical carbon dioxide modifies the properties of ionic liquids, altering the conditions required for optimum enzyme activity. These findings indicate that the combination of ionic liquids with supercritical carbon dioxide may represent a particularly efficacious medium for clean non-aqueous biosynthesis.

Well before the introduction of catalytic reactions in ionic liquids and supercritical carbon dioxide (SC-CO_2), Mother Nature developed enzymatic catalysis in aqueous (fermentation) and non-aqueous (bilayer membranes) media for facile, highly selective, "green" synthesis. Use of enzymes in organic solvents

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has shown significant promise, particularly for the production of chiral pharmaceuticals (*1,2*). Enzymes in organic solvents can have novel synthetic capabilities, altered selectivities and enhanced stability (*2,3*). Exploitation of enzymes in neoteric solvents may bring us full circle in the development of environmentally benign chemical processes.

The most commonly studied enzymes in nonaqueous media are lipases and proteases, which hydrolytically cleave lipids and polypeptides, respectively, under normal operating conditions. In water-restricted environments, these enzymes can catalyze esterifications and amidations.

To maintain their activity, enzymes need to retain a small amount of bound water (*1,4-6*). This sets up a tension between having too much water, thus shifting the reaction towards hydrolysis, and too little water, leading to enzyme inactivation. Nonpolar solvents are generally preferred because they are less likely than polar solvents to strip critical water from enzymes. As unmodified proteins generally lack solubility in nonaqueous fluids, heterogeneous reaction conditions prevail. Enzymes can be added as lyophilized powders or, preferably, immobilized on inert solid supports (*7-11*). Apart from improving mass transfer kinetics of substrates, the support can dramatically influence enzyme catalytic properties. Hydrophobic supports are often preferred, presumably because there is less competition with the enzyme for water. Contrary to this general rule, a few enzymes have shown remarkable increases in activity when associated with amphipathic polymers such as poly(ethylene glycol) or with simple salts such as KCl (*10,12-16*). The influence of these hydrophilic supports on enzyme bound water is less clearly understood. Thus, when investigating new media such as ionic liquids, the role of water in the medium and its impact on enzyme activity needs to be addressed. In aqueous environments, enzyme activity can be acutely sensitive to pH due to its effect on the ionization state of acid/base functional groups in the protein, particularly for residues in the active site of the enzyme. It is widely observed that enzymes retain their protonation state when transferred from an aqueous to a nonaqueous environment, referred to as the "pH-memory" effect (*17*). However, the apparent pH-optimum may be shifted higher or lower in the nonaqueous solvent. These considerations need to be examined with regard to using enzymes in neoteric solvents.

Chymotrypsin, a protease with a substrate specificity for aromatic amino acid residues, has been studied extensively in organic solvents and to a lesser degree in SC-CO_2 (*18-27*). Many of the generalizations discussed above concerning the catalytic properties of enzymes in nonaqueous media have been drawn from studies of chymotrypsin. As such, chymotrypsin may serve as a useful model enzyme to examine in ionic liquids. A typical reaction is illustrated in Figure 1, with chymotrypsin (Ct) catalyzing the transesterification of *N*-acetyl-L-phenylalanine ethyl ester (APEE) with a short-chain primary alcohol (1-propanol, in this case) to produce the propyl ester (APPE).

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An unwanted side reaction is the hydrolysis of the APEE to N-acetyl-L-phenylalanine (APA).

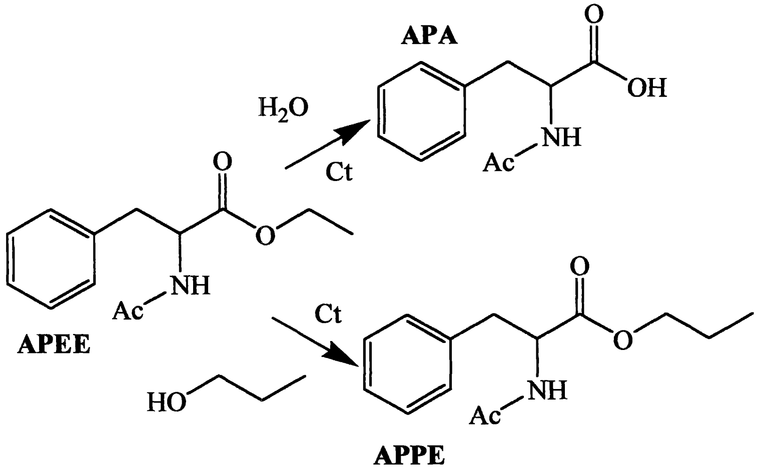

Figure 1. Model transesterification and hydrolysis reactions.

In the present work, we describe how the nature of the ionic liquid, water content, and other factors influence the catalytic activity of chymotrypsin. In addition, we examine the use of SC-CO_2 in conjunction with ionic liquids as a medium for biocatalysis. We will demonstrate that the combination of ionic liquid and SC-CO_2 is mutually beneficial, being more productive than either solvent alone, as well as providing a simple route for the isolation of products. There have been several very recent reports of other enzymatic reactions in ionic liquids (*28-30*). We will compare our findings to these studies.

Methods

The water-immiscible ionic liquids [bmim][PF_6] and [omim][PF_6] (1-butyl- and 1-octyl-3-methylimidazolium hexafluorophosphate, respectively) were synthesized following published methods and brought to dryness (< 0.03% w/w water by Fischer titration) under reduced pressure and heating (*31,32*). Water amounts added back to the ionic liquids are reported on a volume basis.

Chymotrypsin was prepared for use by freeze drying samples in various aqueous buffered salt solutions. Preparations included were: an equal mixture by

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weight of chymotrypsin and K_2HPO_4, pH 7.0, referred to as Ct-K_2PO_4; a preparation consisting of 1% chymotrypsin, 1% K_2HPO_4, and 98% KCL (Ct-KCl); and a preparation with equal parts chymotrypsin, K_2HPO_4, and poly(ethylene glycol) (Ct-PEG) (*13-15*).

Enzyme reactions were conducted in small glass vials equipped with stir bars. Vials were loaded with a particular enzyme preparation (typically 2 mg of Ct) and 4 mL of reaction solution consisting of the substrates APEE (5 mM) and 1-propanol (500 mM) in organic solvent or ionic liquid, and water as needed. Reactions were conducted in an incubator maintained at 40 °C, equipped with a multi-position stir plate. At intervals over 20 to 360 min, the reaction was sampled and analyzed by HPLC (33). Reaction rates (mmol/h · g) were determined by linear regression analysis of product concentrations, not exceeding 10 mol% conversion of APEE to products (APA plus APPE). Rates are reported on an enzyme weight basis.

The apparatus used for enzyme reactions in SC-CO_2 is described by Compton and King (*34*). A 5-mL reaction cell equipped with a teflon stir bar was loaded with enzyme (5.0 mg Ct-PEG), substrates (0.05 mmol APEE, 2.5 mmol 1-propanol), and, in some cases, ionic liquid (2 mL). The reactor was sealed and allowed to thermally equilibrate at 45 °C for 30 min, then adjusted to the desired pressure with CO_2. Reactions were stirred for 4 or 24 h, then cooled to ambient temperature. The reactor was depressurized and its contents were analyzed by HPLC. Yields reported are the average of reactions performed in triplicate and the relative standard deviations of the APEE and APA yields were < 4.0 mol%.

Results and Discussion

Influence of Support and Solvent

The activity of chymotrypsin in ionic liquids was substantially influenced by the material with which the enzyme was immobilized during the freeze drying process, as well as by the type of ionic liquid employed (Table I). With the enzyme immobilized with just phosphate buffer (Ct-K_2PO_4), transesterification was four-fold faster in [omim][PF_6] than [bmim][PF_6]. The activity of Ct-K_2PO_4 in [omim][PF_6] was better than in either acetonitrile, a polar solvent, or the non-polar solvents hexane or isooctane. Chymotrypsin immobilized with a large excess of salt (Ct-KCl) demonstrated no or very low activity in ionic liquids, but improved activity in non-polar solvents compared to the phosphate immobilized enzyme. KCl-encasement has been shown to dramatically increase enzyme activities in non-polar solvents, including that of chymotrypsin (*10,12*). It is possible that the ionic liquids were poorly able to penetrate the KCl particles and reach the enzyme.

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Chymotrypsin chemically modified, or simply physically adsorbed to, poly(ethylene glycol) has been shown to have much higher activity in non-polar solvents than unmodified enzyme. Incorporation of poly(ethylene glycol) into chymotrypsin along with phosphate (Ct-PEG) increased activity three-fold in [omim][PF_6] but did not improve activity in [bmim][PF_6]. The poly(ethylene glycol) was far more effective in improving activity in hexane and isooctane. Poly(ethylene glycol) is highly soluble (greater than 100 mg/mL) in both ionic liquids, yet the enzyme appeared to remain insoluble. It is possible that the ionic liquids may have removed much of the poly(ethylene glycol) from the enzyme, preventing the poly(ethylene glycol) from maintaining the proper hydration state of the enzyme. Chemical modification of the enzyme with poly(ethylene glycol) may be more effective. Poly(ethylene glycol) is also known to be a good lyoprotectant (preserving activity during lyophilization), but this effect would not explain why activity was improved in [omim][PF_6] but not [bmim][PF_6].

Table I. Influence of Solvent and Support on Chymotrypsin Transesterification Rates

	Transesterification Rate (mmol/h · g)		
Solvent	*K_2HPO_4*	*KCl*	*PEG*
Acetonitrile	0.03	0.00	0.35
Hexane	0.08	0.60	5.5
Isooctane	0.16	0.41	5.6
[bmim][PF_6]	0.05	0.00	0.03
[omim][PF_6]	0.19	0.07	0.48

NOTE: See Methods for description of chymotrypsin support types and reaction conditions. Acetonitrile, [bmim][PF_6], and [omim][PF_6] contained 1% (v/v) water.

It is unclear why [omim][PF_6] is a better solvent than [bmim][PF_6] for chymotrypsin catalyzed transesterifications. The stripping of essential water is believed to be a major solvent influence on enzyme actitivity in nonaqueous media. The longer hydrophobic tail of the octyl-imidazolium group of [omim][PF_6] might suggest there would be less water stripped from the enzyme in this solvent. However, both ionic liquids can solubilize similar amounts of water (1.5 and 1.9%

w/w at 25 °C for [bmim][PF_6] and [omim][PF_6], respectively). Solvent dielectric also is considered to play an important role in enzyme activity in nonaqueous solvents (*5,35*), but we expect the dielectric of both ionic liquids to be similarly high. Non-aqueous solvents can impact enzyme activity by direct interactions with protein groups, leading to altered enzyme conformation and activity loss. This would suggest that [omim][PF_6] physically interacts with the enzyme less than [bmim][PF_6]. The conductivity of [bmim][PF_6] is approximately six-fold higher than [omim][PF_6] (determined with a Cole-Parmer Au conductivity probe), indicating that [bmim][PF_6] provides more free ions that are able to associate with the enzyme. More investigation is needed to clarify the role of various potential mechanisms by which the structure of the ionic liquid influences enzyme activity.

Transesterifications conducted in [bmim][PF_6] or [omim][BF_4] catalyzed by *Candida antarctica* Lipase B have been reported recently (*29*). Little difference in enzyme activity was found between the two ionic liquids. It was observed that enzyme immobilization on various polymeric supports improved enzyme activity over that of a lyophilized powder. The synthesis of *Z*-aspartame in [bmim][PF_6] catalyzed by thermolysin, a protease derived from the thermophile *Bacillus thermoproteolyticus rokko*, was examined in [bmim][PF_6] (*28*). The enzyme was added to the reaction as a powder, some of which apparently dissolved in the ionic liquid and was inactivated. They do not describe the influence of any type of immobilization support or other ionic liquid. Therefore, it is unknown whether thermolysin activity would benefit from immobilization, as does chymotrypsin (in [omim][PF_6]) and *Candida antarctica* Lipase B.

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Influence of Ionic Liquid Water Content

The water content of [omim][PF_6] affected chymotrypsin transesterification and hydrolysis rates (Table II). No activity was observed in dry (< 0.01% water) [omim][PF_6]. With water added, both hydrolysis and transesterifaction rates increased until the water content was 0.5%, then decreased with additional water. At the optimum water content, the Ct-PEG transesterification rate in [omim][PF_6], was one-third of the rates observed in hexane or isooctane. The ratio of hydrolysis to transesterification rose with increasing water content of the solvent. A bell-shaped activity curve has been observed with chymotrypsin and other proteases in various organic solvents and condensed gases (*36-39*). Water concentrations in the solvent below the optimum may leave the enzyme under hydrated, while above the optimum the enzyme achieves a flexibility sufficient to allow denaturation.

Transesterifications catalyzed by *Candida antarctica* Lipase B were rapid and in high yield in anhydrous ionic liquid (*29*). This lipase has very low water requirements for activity, unlike chymotrypsin. Thermolysin-catalyzed synthesis of *Z*-aspartame in [bmim][PF_6] was conducted with 5% water (*28*). As lower water concentrations limited the solubility of substrates and products, they were unable to determine the influence of water content in the solvent on enzyme activty. Thus, it is likely that each combination of enzyme, support, and reaction will have its own unique water requirement for optimal activity in ionic liquids.

Influence of Aqueous pH

Enzymes in aqueous media have distinct pH values at which they are most active. Enzymes prepared for use in organic solvents (by freeze drying or other means) tend to retain the protonation state established in the aqueous buffer, and thus will have similar pH optima in an organic solvent. Studies with chymotrypsin in organic solvents have indicated there is a one to two pH unit alkaline shift in the optimum (*23,27*). Chymotrypsin in [omim][PF_6] demonstrated a broad transesterification activity optimum between pH 6 and 8 (Figure 2). In aqueous media the activity optimum is pH 7.8 (hydrolysis reaction). Thus, unlike conventional organic solvents, the pH optimum of the enzyme is not shifted in ionic liquids. The drop off in transesterification activity below the pH optimum is not as rapid in [omim][PF_6] as that observed in either aqueous or organic media (*23,27*), whereas there was a far greater decrease in hydrolysis activity at pH 6 (data not shown). These unusual features of the pH dependency of chymotrypsin activity will require additional investigation in order to provide an explanation for this behavior. No pH effects have been reported for lipase or thermolysin activity in ionic liquids.

Influence of Supercritical Carbon Dioxide on Reaction Rates and Product Yields

The activity of chymotrypsin was investigated in reactions containing ionic liquids with SC-CO_2 as a cosolvent. SC-CO_2 is an environmentally benign solvent that is highly soluble in [bmim][PF_6] and [omim][PF_6], reaching mole fractions of 0.6 and 0.8, respectively, at 10 MPa and 50 °C (*40, 41*). Figure 3 shows the yields of the transesterification and hydrolysis products obtained from the reaction of APEE with 1-propanol in ionic liquid/SC-CO_2 solutions (13.8 MPa, 45 °C) catalyzed by Ct-PEG. The transesterifications identified as dry denote reactions containing ionic liquid with < 0.03% (w/w) water, and reactions denoted as wet contained ionic liquids with 1% (v/v) water added.

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Table II. Influence of Water Concentration on Ct-PEG Transesterification and Hydrolysis Rates in [omim][PF$_6$]

Water (% v/v)	*Transesterification* (*mmol/h · g*)	*Hydrolysis* (*mmol/h · g*)
0.25	1.2	0.27
0.50	1.8	0.58
0.75	1.0	0.45
1.00	0.48	0.38

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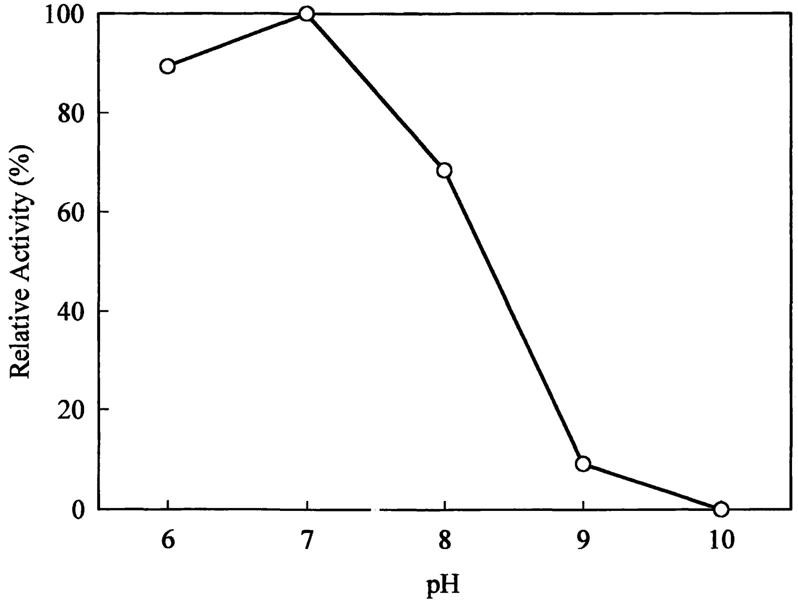

Figure 2. Effect of aqueous pH on Ct-PEG transesterification activity in [omim][PF$_6$] containing 0.5% (v/v) water. Maximum activity was 1.8 mmol/h·g.

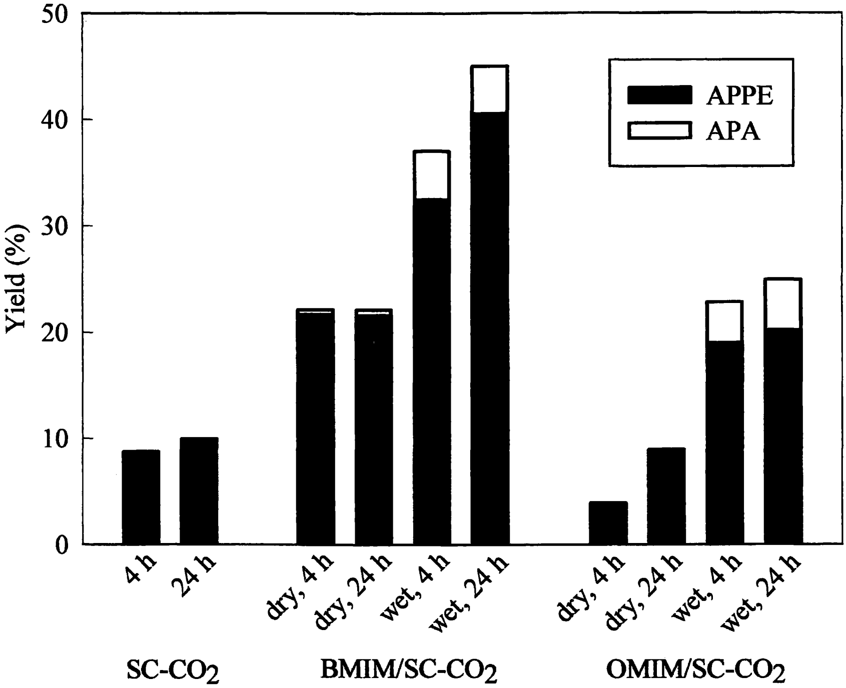

Figure 3. Influence of ionic liquids on the reaction of APEE with 1-propanol catalyzed by Ct-PEG performed in SC-CO_2 (13.8 MPa, 45 °C). Dry reactions contained ionic liquids with < 0.03% (w/w) water and wet reactions contained ionic liquids with 1% (v/v) water.

The reactions performed in dry ionic liquid/SC-CO_2 solutions demonstrate that Ct-PEG activity does not require additional water as was needed for the reactions performed in neat ionic liquids. This suggests that the ionic liquid/SC-CO_2 media strips less water from the Ct-PEG enzyme complex. The relative rates of the dry reactions show that the [bmim][PF_6]/SC-CO_2 medium promotes faster turnover and higher APPE yields than [omim][PF_6]/SC-CO_2 or neat SC-CO_2. The [omim][PF_6]/SC-CO_2 solutions produced the same APPE yields as those obtained in control reactions containing no ionic liquid. It is unclear why [omim][PF_6]/SC-CO_2 results in lower reaction rates and yields. There was little change in product

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yield over a 13.8 to 34.5 MPa pressure range with the [bmim][PF_6]/SC-CO_2 medium (data not shown).

Although additional water is not needed for Ct-PEG activity, additional water does increase the rates and yields of the transesterifications performed in ionic liquid/SC-CO_2. Figure 3 illustrates that increasing the water content of the ionic liquids to 1% (v/v) doubled the APEE yields after 24 h for reactions performed in both [bmim][PF_6]/SC-CO_2 and [omim][PF_6]/SC-CO_2. Again, [bmim][PF_6]/SC-CO_2 was the superior media with double the reaction rate and APPE yield compared to reactions performed in [omim][PF_6]/SC-CO_2. These findings are contrary to the transesterifications performed in the neat ionic liquids where [omim][PF_6] proved to be the superior solvent.

Conclusions

Ionic liquids appear to be potentially useful media for conducting non-aqueous enzymatic reactions. What is already known about the behavior of enzymes in conventional molecular solvents will serve as a valuable guide to those who study enzymes in neoteric solvents, but, as demonstrated in this work, there will be unanticipated differences. As with conventional organic solvents, the interaction of the enzyme with water in ionic liquids is a critical consideration. Chymotrypsin displays a pronounced activity dependence on water activity and pH in an ionic liquid, as it does in other non-aqueous fluids. Conversely, certain enzyme support media such as PEG and KCl, which can greatly improve enzyme performance in conventional molecular solvents, appear less helpful in ionic liquids. Chymotrypsin displays a clear preference between the two different cations comprising the ionic liquids used in the present work. Lacking a definitive characterization of the physical properties of these ionic liquids at this time, drawing a conclusion as to the nature of this cation preference is not possible. Supercritical carbon dioxide will be a useful adjunct to enzymatic catalysis in ionic liquids, whether it is employed to separate reaction products from the medium or to improve the mass transfer kinetics of substrates. The present work demonstrates that the use of enzymes directly in ionic liquids/SC-CO_2 media is feasible, but inclusion of the supercritical phase substantially alters chymotrypsin's water requirements and cation preference.

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Chapter 31

Small-Angle Scattering from Long-Chain Alkylimidazolium-Based Ionic Liquids

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This paper compares the structure of 1-alkyl-3-methylimidazolium salts using SAXS and X-ray reflectivity. A range of anions have been investigated namely chloride, bromide, trifluoromethanesulfonate (OTf), *bis*(trifluoromethanesulfonyl)imide (TFI) and tetrachloropalladate(II) with cation alkyl chains ranging from *n* = 12-20. In general, the salts show liquid crystalline behaviour whose structure is still observed on melting into an isotropic liquid.

Room-temperature ionic liquids have been utilised as clean solvents and catalysts for green chemistry (*1*) and as electrolytes for batteries, photochemistry and electrosynthesis (*2*), each of which have been extensively reviewed. Interest in this class of solvent stems from the properties exhibited by the liquids (including effectively zero vapour pressure) and the ease by which many of their physical properties may be varied (*3*). Currently, the ionic liquids of choice for these applications comprise of an organic cation, for example 1,3-dialkylimidazolium cations (*4*) (Figure 1) with a wide variety of anions (*5*-*7*). By lengthening one of the alkyl-chain substituents of the 1-alkyl-3-methylimidazolium cation, large changes in the physical properties of the

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resultant ionic liquids can be achieved (*8*). These include changes in viscosity and density as well as the ready formation of thermotropic liquid crystal mesophases (*9*) for long-chain salts. These latter salts resemble those of related *N*- alkylammonium salts previously reported by, for example, Busico *et al.*(*10*).

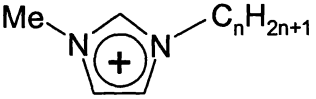

Figure 1 The general structure of 1-alkyl-3-methylimidazolium cation for the salts studied (n = 12-20).

Amphiphilic ionic salts have many applications for example, templating mesoporous materials (*11*), the formation of ordered films (*12*), as ionic liquid crystals (*10,13*) and ionic metallomesogens (*14,15*). In the latter, metal-containing moieties can be introduced as either the mesogenic unit (*16*) or as the counter ion.(*17,18*)

In this paper, we present SAXS and X-ray reflectivity data for a range of 1-alkyl-3-methylimidazolium salts with chloride, bromide, trifluoromethanesulfonate (OTf), *bis*(trifluoromethanesulfonyl)imide (TFI) and tetrachloropalladate(II) anions. The structure of the salts described are compared and show a common motif in both the crystal and liquid crystalline phases which, in the latter case, is still present in the liquid structure.

Experimental

The salts were prepared from the corresponding 1-alkyl-3-methylimidazolium chloride salts by metathesis using established literature procedures (*5-8*). Each salt was purified by recrystallisation and characterised by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy and differential scanning calorimetry (DSC). In each case the purity was greater than 99.5% estimated from elemental analysis. The melting points, DSC traces and polarizing optical microscopy for each salt studied is detailed in references 5 and 20.

Variable temperature small angle X-ray scattering (SAXS) experiments were carried out at the SRS, Daresbury, UK on beamline 8.2. Data were obtained from the salts in sealed 1 mm glass Lindemann tubes using a monochromated (1.54 Å) X-ray beam. Samples were transferred to the Lindemann tubes as molten liquids. A multiwire quadrant detector was used with camera length of 0.95 m, effective range 8 - 190 Å. Heating was achieved using a Linkam hot stage. The detector was calibrated with silver behenate(*19*).

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The X-ray reflectivity experiments were carried out at the SRS in Daresbury, U.K., on station 16.2. The X-ray beam was monochromated to 1.36 Å and data was collected over the incidence angle range 0-5°. Samples were spin coated from methanol solutions onto cleaned, polished Si(111) wafers In each case, the samples were annealed above the respective melting points of the samples and the measurements taken on the thermally treated films.

The details of the analysis and methods used have been published previously for both the SAXS (*5*,*20*) and X-ray reflectivity measurements (*21*).

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Results

Small Angle X-ray Scattering

Non-metal containing 1-methyl-3-alkyl imidazolium salts.

Figure 2 shows typical SAXS data for the salt [C_{16}-mim][OTf]. This is a specific example of the more general pattern found for all the non-metal salts studied, *i.e.* for Cl^- , Br^-, $[OTf]^-$, $[TFI]^-$ and $[BF_4]^-$. Each of the salts shows at least one peak in the small angle region and diffraction patterns which are consistent with a lamellar structure containing charged layers separated by hydrocarbon chains in both the crystal and liquid crystalline phases. Table 1 summarises the interlayer spacing, *d*, based on the lowest angle feature in the SAXS data on cooling from the liquid phase. The interlayering spacing was calculated using Bragg's law.

For those salts showing a liquid crystalline phase, the SAXS pattern in the mesophase consists of a sharp peak between $2\theta = 1–5^\circ$, *i.e.* the phase has an interlayer spacing between 22-61 Å. As expected the interlayer spacing increases uniformly with increasing alkyl chain length, *n*, however the variation with anion is more complex. For a given cation the mesophase interlayer spacing decreases following the order $Cl^- > Br^- > [BF_4]^- > [\ OTf]^-$ with the *bis*(trifyl)imide salts not exhibiting any mesophase structure.

In the crystal phase, the SAXS data contains more features. In general, more than one phase is displayed but this is highly dependant on the thermal history of the samples. In the majority of the non-metal salts studied, an intense

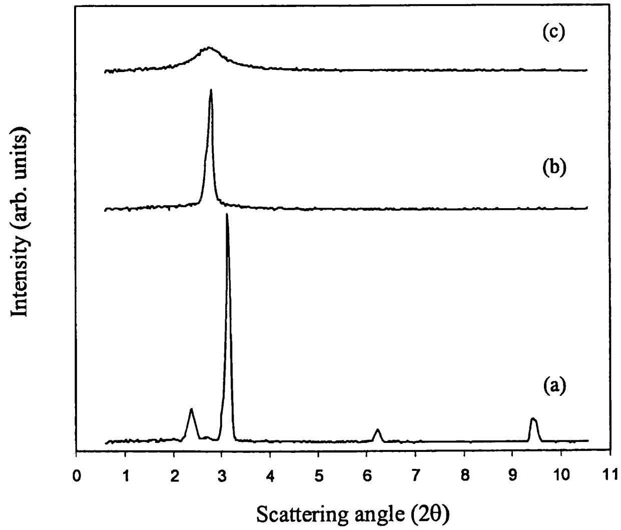

Figure 2 SAXS pattern for [C_{16}-mim][OTf] at (a) 50 °C, (b) 70 °C and (c) 90 °C, in the crystal, SmA_2 and isotropic phases respectively, on cooling.

feature is displayed between 2θ = 2.8–3.9°. Taking this feature as the (001) interlayer repeat, on transforming from the crystal to the mesophase, the interlayer spacing increases for all the salts studied. This is clearly shown in Figure 2(a) and (b), where the (001) peak is shifted from 3.12 ° to 2.79° with increasing temperature, corresponding to a increase in the interlayer spacing from 28.2 Å in the crystal phase to 31.6 Å in the mesophase. This is not unusual for surfactants molecules.

Some of the salts, specifically those containing halide, also exhibit SAXS peaks below 2°. This is illustrated in Figure 3 for [C_{18} -mim]Cl. In this case, an intense peak is observed at 1.45° corresponding to a *d* spacing of 60.9 Å. However, the presence of the large interlayer spacing is not reversible, after one heating-cooling cycle the feature disappears and is replaced by a single feature at 2.85° (*d* = 31.0 Å) in line with the diffraction patterns for the other salts.

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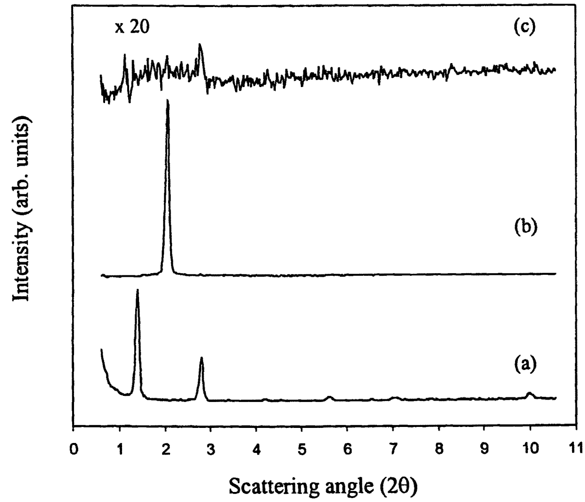

Figure 3 SAXS pattern for [C_{18}-mim]Cl at (a) 30 °C, (b) 75 °C and (c) cooled back to 30 °C, i.e. in the crystal, liquid crystal and back to the crystal phases, respectively.

For all the non-metal salts studied, the SAXS data also shows smaller features in the crystal phase. For example, in Figure 2, peaks are observed at 2.45°, corresponding to a periodicity of 36.0 Å, and in the wider angle data at 9.40°, corresponding to 9.4 Å. In all cases, these peaks are much less intense and do not fit the regular repeat unit of the layered structure (determined from the (001) and (002) peaks at $2\theta = 3.15°$ and 6.30°, respectively). The wider angle feature corresponds to the cation–cation and anion–anion repeat distance within the charged region. This feature is only present in the initial crystal structure, on cooling from the liquid phase, the peak disappears indicative of a reduction in the positional ordering within the layer.

On melting to the isotropic liquid, a broad peak is observed in the SAXS data for each salt. This peak indicates that even within the isotropic liquid phase, some short-range associative structural ordering is still retained.

Palladium containing 1-methyl-3-alkyl imidazolium salts.

For the palladium containing salts, the SAXS data for all alkyl chain lengths studied showed similar patterns consistent with a layered structure as observed for the non-metal containing salts. Table 1 also summarises the interlayer spacings found for the palladium based salts.

In the room temperature crystal phase, peaks are observed at low angle, $2\theta = 1.58$–1.87°. These correspond to (001) interlayer spacings of between 47-

Table 1 Summary of (001) interlayer(d / Å) spacings determined from SAXS data, based on the lowest angle scattering peak.

n	*Anion*	*Phase*			
		Crystal			*Liquid Crystal*
12	$[TFI]^-$	24.7			-
14		25.2			-
16		28.2			-
18		28.8			-
12	$[OTf]^-$	26.8			-
14		29.4			-
16		28.2 (36.6[a])			31.7
18		30.3 (43.4[a])			34.4
12	$[BF_4]^-$	-			-
14		27.2			31.4
15		28.6			33.0
16		32.1			35.4
18		34.6			37.7
12	Cl^-	22.5	-		31.7
14		50.7[b]	25.8		34.4
16		56.6[b]	29.0		36.6
18		60.9[b]	31.0		41.2
12	Br^-	22.8	-		32.0
14		53.5[b]	27.0		33.6
16		30.7	-		36.3
20		31.6	-		38.8
12	$[PdCl_4]^{2-}$	47.1[b]	31.9	33.0	-
14		50.1[b]	35.2	37.2	30.3
16		55.8[b]	37.6	39.9	33.2
18		-	41.1	43.4	35.4

[a] low intensity peak associated with periodicity along the alkyl chain director.

[b] initial crystal phase observed on first heating only.

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56 Å. Figure 4 shows the variation in the SAXS pattern with temperature for $[C_{14}\text{-mim}]_2[PdCl_4]$ as a typical example. In this pattern, two other peaks are shown, the second order diffraction peak at 3.52° and a weaker peak at *ca.* 8.25°, which corresponds to a periodicity of 10.6 Å. The latter is associated with the $[PdCl_4]^{2-}$ to $[PdCl_4]^{2-}$ anion correlation distance.(*17*,22)

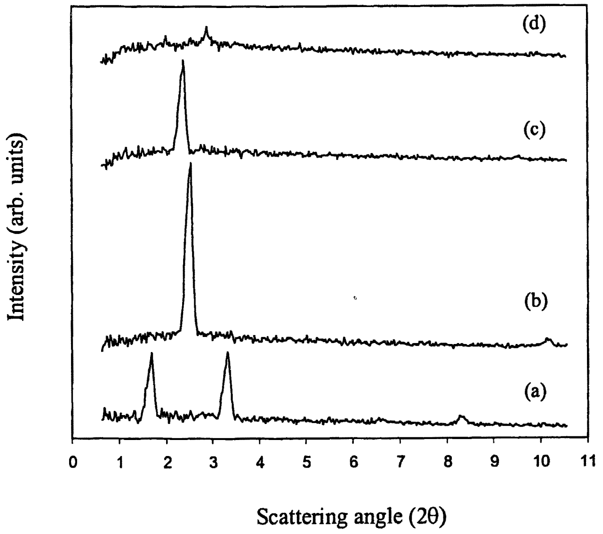

Figure 4 SAXS pattern for $[C_{14}\text{-mim}]_2[PdCl_4]$ at (a) 50 °C, (b) 85 °C and (c) 110 °C and (d) 140 °C from first heating.
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On heating $[C_{14}\text{-mim}]_2[PdCl_4]$ to 78 °C, an irreversible phase change occurs from Cr to a higher temperature Cr' phase. In the Cr' phase, the low angle feature disappears and a single peak is observed at 2.51°, corresponding to a (001) layer spacing of 35.2 Å. A shift to higher angle is also observed in the wide angle features, corresponding to a decrease in the anion-anion correlation from 10.6 Å to 8.7 Å.

At 100 °C, the salt undergoes a second crystal-crystal transition to a Cr" phase, indicated by a small shift in the (001) peak to lower angle. In Figure 4, the peak shifts from 2.51° to 2.37°, *i.e.* an increase in the (001) layer spacing from 35.2Å to 37.2 Å. For all the palladium salts studied, transforming from the Cr' to Cr" phase results in the loss of the higher angle reflection associated with the anion-anion correlation.

Above 120 °C, the Cr" phase melts to a liquid crystalline phase with the (001) peak shifting to higher angle due to a contraction of the interlayer spacing. For $[C_{14}\text{-mim}]_2[PdCl_4]$, the interlayer spacing decreases from 37.2 to 30.3 Å.

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This phase change is accompanied by a marked decrease in intensity and broadening of the (001) peak. No liquid crystalline phase was observed for $[C_{12}\text{-mim}]_2[PdCl_4]$.

The latter two phase transitions (*i.e.* Cr'-Cr" and Cr"-liquid crystal) are fully reversible on cooling. However, in all cases the structure remains in the Cr' phase on cooling.

X-Ray Reflectivity

Table 2 summarises the X-reflectivity data exhibited by palladium containing and non-metal long alkyl chain imidazolium salts. In each cases, the periodicity data extracted from patterns is derived from thermally treated films. The untreated spin coated samples showed a featureless profile due to the films being rough. After melting to the liquid and cooling, smooth ordered films were produced with thickness ranging from 100-210 Å as determined from the minimum in Q_z. For all the salts studied, Bragg features were clearly visible, however, in most cases, the additional Kiessig fringes which allow the structure within the film and at the interfaces to be determined were not evident. The Bragg peaks indicate an ordered local structure within the sample film and the interlayer spacings, determined from the position of the first Bragg peak, are given for the solid and liquid crystalline films.

For each salt, the films have periodicities which are similar to those found for the bulk samples. In general, the films exhibit a slightly larger distance than in the bulk samples, for example $[C_{18}\text{-mim}][PF_6]$ reflectivity gives 29.5 Å whereas 27.7 Å is determined from X-ray diffraction on the bulk sample. It should be noted that in the case of the $[C_{12}\text{-mim}]_2[PdCl_4]$ film, the long range periodicity observed in the SAXS data is not observed in the thin films due to the samples being thermally treated and this initial transition was only observed in the SAXS for the untreated sample. In this sample, two Bragg features were observed on cooling through the intermediate crystal phase from the isotropic liquid to the room temperature crystal phase corresponding to a mixed phase of two crystal phases with periodicities of 30.7 Å and 33.1 Å. The latter corresponds to the low temperature phase and has a periodic spacing greater than that for the thermally treated bulk samples, *i.e.* in the Cr' phase.

For the $[PF_6]^-$ and $[BF_4]^-$ films, the liquid crystalline phases show an increased layer spacing compared with the solid as was observed in the SAXS data.

Kiessig fringes were observed in addition to the Bragg feature for the $[C_{18}\text{-mim}][PF_6]$ salt. These were present in both liquid crystalline and solid phases, however, they were more pronounced in the latter. The details of the Kiessig fringes is beyond the scope of this paper but is presented in reference 21, an example of the data obtained is shown in Figure 5

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Table 2 Summary of interlayer (*d* / Å) spacings determined from X-ray reflectivity data, based on the lowest Bragg peak.

n	*Anion*	*Phase*		
		Crystal[a]	*Liquid Crystal*	*Bulk Crystal*[b]
18	$[BF_4]^-$	34.7	36.5	34.6
12	$[PdCl_4]^{2-}$	33.1 / 30.7	31.8[c]	31.9
12	$[PF_6]^-$	23.4	-	22.4
18		29.5	34.5	27.7

[a] Thermally treated films, pre-melted prior to measurement.

[b] Determined from SAXS and XRD data on salt crystallized from the melt.

[c] Crystal-crystal transition, no liquid crystalline phase present.

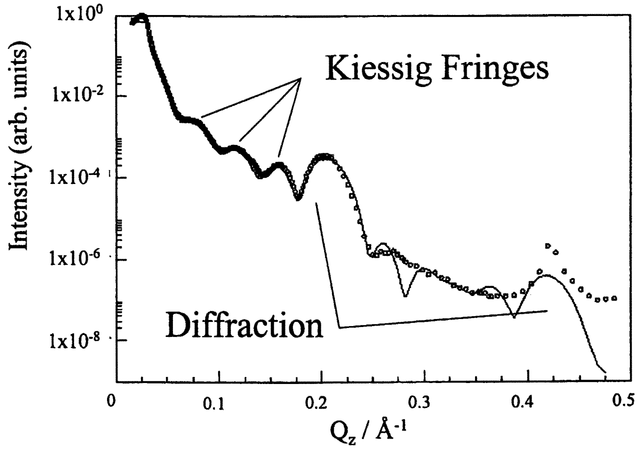

Figure 5 Experimental reflectivity data (points) compared with a 5 bilayer model (solid line) for a 156 Å thick $[C_{18}\text{-mim}][PF_6]$ films at 298 K. . (Reproduced with permission from reference 21. Copyright 2001.)

Discussion

The structure of all the salts studied are similar and consist of charged layers of anions and cations separated by regions of alkyl chains consistent with the X-ray single crystal structure of [C_{12}-mim][PF_6] (*6*). In general, the *d* spacings in both the crystal and liquid crystalline phases for all the salts studied lie between *l* and *2l*, where *l* is the fully extended alkyl chain length. This indicates that in both phases, the alkyl-chains of the cations are interdigitated and/or tilted with respect to the layer normal. POM measurements (*5,20*) on all the liquid crystalline phases indicate that there is no angular alignment within the hydrocarbon region consistent with a thermotropic smectic A assignment and thus interdigitation must be present.

The general phenomena that the layer spacing increases, on transforming from the crystal to the mesophase in the non-metal containing crystals, indicates that not only do the alkyl chains melt but the structure also undergoes a conformational change, for example decreasing the angle of tilt with respect to the layer normal. In the palladium containing salts, a decrease in the layer spacing is found on forming the liquid crystalline phase. In this case, if the alkyl chains are tilted, any conformational change is of secondary importance compared with the alkyl-chain melting.

The tetrachloropalladate salts, show crystal polymorphism which is not found at the temperatures studied for the non-metal containing salts, in general. In the palladium salts, the large periodicity found at room temperature is approximately twice the molecular length (*l*) of the fully extended cation (for $n = 14$; $d = 52.1$ Å and $l = 26$ Å, based on molecular models). Two models can be proposed to explain this periodicity,

(i) a lamellar, bilayer structure with no alkyl-chain interdigitation, *i.e.* end to end packing of the alkyl chains or

(ii) a double bilayer structure where the conformations of the head-groups in alternating layers is different.

Although it is not possible to distinguish the two scenarios using the data presented here, it is more likely that the interdigitated structure is formed.

Some crystal polymorphism is also shown by the halide salts. As with the tetrachloropalladate salts, [C_n-mim]Cl ($n = 14, 16, 18$) and [C_{14}-mim]Br show a large periodicity in the room temperature crystal structure. This structure is not stable with respect to temperature and collapses to a much smaller spacing on cooling from the liquid.

In both the halide and tetrachloropalladate salts, these initial crystal structures may be considered as unusual and are due to a solvent induced crystal structure as opposed to ones nucleated from the melt. In this case (i) would simply revert to a structure where interdigitation was present whereas in (ii) the charged region would have similar conformations of the head-groups in

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alternating layers. It should be noted that for all salts studied the signal-to-noise on cooling from the liquid or liquid crystalline regions is much reduced, as shown in Figure 3(c). This indicates that the liquid crystal undergoes a glass transitions and although some order is present, it decreases on thermal crystallisation compared with solvent crystallisation.

A layered structure is consistent with the Bragg diffraction found in the thin films as determined by X-ray reflectivity. The gross features are reproduced compared with the bulk samples with only minor shifts in layer spacing. The small changes in layer spacing are likely to be due to the thin film structure not being constrained by long range order effects and hence adopts a slightly different lower energy form. The structure found is likely to be substrate dependant as the orientation of the charged groups on the surface will determine how the molecules pack. The similarity between the bulk samples and the thin film is further exemplified from the modeling of the Kiessig fringes in the case of [C_{18}-mim][PF_6]. Here, the data were modeled using a volume fraction based on the periodic bilayer structure in the crystal structures of long-chain alkylimidazolium salts (*6*) was used. This model was comprised of layers of associated 1-ethyl-3-methylimidazolium cation head groups and hexafluorophosphate anions, denoted as the charged region, separated by hydrocarbon-chains. Reasonable fits were only obtained with the charged region at both the salt-silicon and salt-air interfaces.

The *d* spacing in the mesophase and whether or not a mesophase forms is is determined by the anion-cation interactions within the polar region. In general, the *d* spacing increases $Cl^- > Br^- > [BF_4]^- > [OTf]^- > [TFI]^-$ which follows the anion ability to form hydrogen bonds in a three dimensional lattice. The order may also be determined from the charge density of the anion. However, this simple criterion needs to be qualified since not all the anions looked at are pseudo-spherical, with a total distributed charge density. For example, although the overall charge density for trifluoromethanesulfonate is likely to be lower than for tetrafluoroborate, the charge is localized on the oxygen and therefore the local charge will be higher. It is therefore necessary to add a second argument concerning the accessability of the charge in order to explain the variation observed.

The indication of order in the liquid structure which is similar to that found in the crystal and mesophases allows inferences to made about the liquid stucture packing from the solid state and liquid crystalline data. In this study, it could be argued that the ordering in the liquid is simply a consequence of the long alkyl chains. However, similar results have also been noted for dimethyl imidazolium chloride using neutron scattering (*23*). In this case the crystal structure shows that the chloride is associated with the ring hydrogens of the imidazolium ring and the closest contact between the cations is methyl hydrogen to methyl hydrogen. Although the distances are expanded in the neutron scatteing of the

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melt, these features are reproduced in the liquid phase. This order is present out to at least two shells of chloride.

Conclusions

All the diffraction patterns are consistent with a lamellar bilayer structure where the charged species are separated by indigitated and, in general, tilted alkyl chains. In general, the long alkyl chain imidazolium salts form liquid crystalline phases denoted as smectic A, however the interlayer spacings found are dependant on both the alkyl chain length of the cation as well as the anion type. Some polymorphism is found in the crystal phase but this generally only occurs with the tetrachloropalladate anion. For certain halide and tetrachloropalladate salts, solvent induced crystallization results in a metastable phase with a large periodicity. However, this phase irreversibly transforms on heating and the stable thermal induced crystallization fits with the general trends found for all the other salts studied.

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Chapter 32

Structure–Property Relationships in Ionic Liquids

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Abstract: The structure of an ionic liquid directly impacts its properties. A perspective on the structure of ionic liquids is given with a consideration of the impact of size, shape and charge distribution on the coulombic interactions between the constituent ions. Dramatic changes in structure of molten salts, described as metallotropism, can be affected by the relative AX/MX_m composition, as well as by the choice of templating cations. Solid-state structures of low melting salts provide the foundation to understand structural principles governing the organization of ions in the liquid phase.

Introduction

It is well known that the characteristic properties of ionic liquids can be significantly varied by the choice of anions and cations. To exploit this tunablilty of ionic liquids as solvents it is necessary to understand those forces that give rise to specific properties such as the melting point, polarity and solubility. Undoubtedly these properties are strongly influenced by the structure of the respective ionic (and/or molecular) species in the liquid. In their recent

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review Wasserscheid and Keim summarized the influence of the local structural properties of anions and cations on properties such as melting point, vapor pressure, thermal stability, density, viscosity, solvation strength and acidity (*1*). The size, charge, and distribution of charge of the respective ions are the origin of many of these properties in an ionic liquid. To further understand the structure property relationships in ionic liquids it is important to look beyond the local structure of the respective ions to the structural organizations in the bulk liquid. Significant randomness in organization is necessary to describe the structure of a liquid. However, a majority of materials exhibit only a 10-15% volume expansion on going from the crystalline to the liquid state. Since volume increases with the cube of distance the relatively small volume increase upon melting requires that atom-atom or ion-ion distances in the liquid state are not significantly different from those in the solid state. This is born out in the analysis of numerous X-ray and neutron scattering experiments in liquids as diverse as NaCl (*2*) and SiO_2 (*3*). Thus, it is possible to gain insight into structure property relationships in ionic liquids from a consideration of structural organizations in the solid and liquid state.

A unique class of liquids are ambient temperature ionic liquids, whose properties present a variety of curious features that can begin to be understood from a consideration of the liquid structure. Based on a freshman chemistry understanding of ionic interactions, salts, the combination of anions and cations are expected to have high melting points. Yet as is now apparent from the field of ionic liquids, numerous salts have melting points well below room temperature. While it might be expected that molten salts should dissolve ionic species, Rogers et. al. found that a variety of ionic dyes were partitioned into an aqueous layer whereas when neutral they partitioned into the ionic liquid (*4*). This raises the question as to what determines solubility in a molten salt? And while polarity is an important concept for the synthetic chemist, the measurement of polarity and its impact on the solvent characteristics of molten salts remains a matter of significant discussion. These curious properties are directly related to the structural organization in the melt.

On the Melting Point of Salts

The dominant force of attraction between ions that must be overcome upon melting a salt to an ionic liquid is the coulombic attraction between oppositely charged particles (Coulomb's law).

$$F = \frac{q_1 q_2}{\varepsilon r^2}$$

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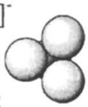
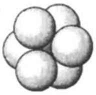
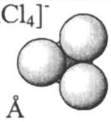
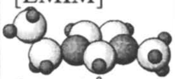
However two features distinguish those salts that exhibit relatively low melting points from those with quite high melting points. In low temperature melting salts, the charge, q, on the ions is normally ±1; and the size of the ions is large, thus the distance, r, separating them must also be relatively large.

In ambient temperature ionic liquids the small charge and large distance reduces the coulombic attractions to a magnitude similar to that of intermolecular interactions in molecular liquids. The size of the respective cations not only decreases the Coulombic attraction by separating the centers of charge, but often the charge in a polyatomic ion will be delocalized over the surface (or volume) of the anion resulting in a dramatically reduced charge density. Comparison of the melting points of the sodium salts in Table 1 serves to demonstrate this effect. On increasing the thermochemical anionic radius from Cl^- < $[BF_4]^-$ < $[PF_6]^-$ < $[AlCl_4]^-$ the melting point of the sodium salts is dramatically reduced from 801 °C to 185 °C.

Table 1: Relative Size of Ions and Melting Points of Salts

Ion	Cl^-	$[BF_4]^-$ 	$[PF_6]^-$ 	$[AlCl_4]^-$ 
Radius surface area volume	1.7Å 36 $Å^2$ 20 $Å^3$	2.2 Å 61 $Å^2$ 45 $Å^3$	2.4 Å 72 $Å^2$ 58 $Å^3$	2.8 Å 98 $Å^2$ 92$Å^3$
$[Na]^+$ 1.2Å 18$Å^2$ 7$Å^3$	801 °C [a]	384 °C (d) [a]	>200 °C [a]	185 °C [a]
$[EMIM]^+$  2.7 × 2Å >80$Å^2$ >46$Å^3$	87 °C [b]	15 °C [c]	58 - 60 °C [d]	7 °C [b]

a. CRC handbook of Physics and Chemistry, b. ref (*1*), c. ref (*7*) d. ref (*6*).

Similarly increasing the size of the cation from Na^+ to 1-ethyl-3-methylimidazolium results in a further decrease in the melting temperature of the respective salts (Table 1). The charge distribution within the EMIM cation

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(EMIM = 1-ethyl,3-methyl-imidazolium), however is not spherical (*5*). The acidity of the hydrogen bound to the C2 of the imidazolium cation is commonly noted. Though less acidic, a partial positive charge, δ^+, also resides on the hydrogens bound to C4 and C5, as is common to all aromatic rings. In contrast to the normally observed δ^- charge on the face of an aromatic ring, some of the positive charge of the imidazolium cation is also distributed over the face of the ring, consistent with resonance structures that assign a positive formal charge to the nitrogens. (Calculations which describe a negative charge for nitrogen, a result of its greater electronegativity, do not differentiate between polar bonds in the σ- and π-systems. It is the removal of one π-electron that gives the immidizolium ring aromaticity and the positive charge.) Examination of the crystal structure of [EMIM][PF_6] (*6*) finds the close contacts between the anions and cations to be associated with the two nitrogens and the three aromatic hydrogens of the imidazolium ring (see below). Thus from a simple consideration, the positive charge of the imidazolium cation can be considered to be distributed over a cylinder defined by the imidizolium core. The alkyl groups bound to the ring increase some cation/anion distances, but these do not significantly participate in charge delocalization. However, in addition to the large size the asymmetrical shape of the EMIM cation disfavors crystallization such that salts with melting points well below room temperature are frequently observed (Table 1). Interestingly, the reported melting point for the [EMIM][PF_6] salt is higher than might be predicted from a simple trend based on anion and cation sizes. This may in part be due to a r_+/r_- radius ratio that favors crystal formation, and hence crystals suitable for a structure determination were obtained.

The composition of the ionic liquid also has a major impact on the observed melting temperature. In a binary mixture, A + B, a maximum in the liquidus is observed at the compositions of specific compounds; for example compound AB as described in the qualitative binary phase diagram in Figure 1.

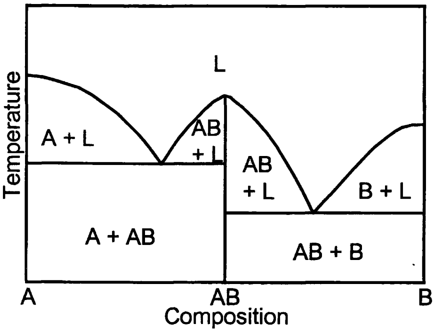

Figure 1: Schematic of a binary phase diagram with a single compound

Deviation from the AB composition results in a lowering of the melting temperature until the minimum observed at the eutectic composition. Such compositional variation is anticipated for most metal-halides that are observed to form low temperature ionic liquids. For example, in the chloroaluminate system $[AlCl_4]^-$, $[Al_2Cl_7]^-$, $[Al_3Cl_{10}]^-$ $[Al_4Cl_{13}]^-$ have been described, although only the 50% composition results in the formation of a compound [EMIM]$[AlCl_4]$ according to the phase diagram (*7*). In this [EMIM][Cl]/$AlCl_3$ binary system eutectics at approximately 38% and 66% result in liquids with melting points (or glass transitions) below -70 °C. A more complex phase diagram has been reported in the [HPy]/$ZnCl_2$ system with compounds reported at 20, 33, 50 and 66 mole percent (*8*). We have also demonstrated this compositional variation in the new class of metallotropic liquid crystals of $ZnCl_2$ with cationic surfactants, which exhibit at least two distinct crystalline phases and a variety of liquid crystalline phases over the composition range of 0 to 85 mole % $ZnCl_2$ (*9*). Similar eutectic behavior can be expected for all salts $[M_nX_m]^{x-}$ anions (e.g. $[F^-]$ $[PF_6]^-$, $[PF_5]^-$, $[PF_3]$ or $[Cl]^-$, $[CuCl_4]^{2-}$, $[Cu_2Cl_6]^{2-}$ …$[Cu_mCl_{2m+2}]^{2-}$, $CuCl_2$). Furthermore, this eutectic behavior accounts for the fact that small deviations in preparations of ionic liquids can result in liquids with significantly different melting temperatures.

Polarity of Salts

The coulombic interactions, described in the previous section, are responsible for the attractive forces that hold anions and cations into a crystalline lattice. Unlike covalent bonds however, these ionic interactions are not directional. Rather in the salt, anions and cations are arranged in space so as to cancel the build-up of charge throughout the bulk material. For example in the well known NaCl structure, Figure 2, no NaCl molecules exist, rather each sodium cation is surrounded by six nearest neighbor chloride anions, and each

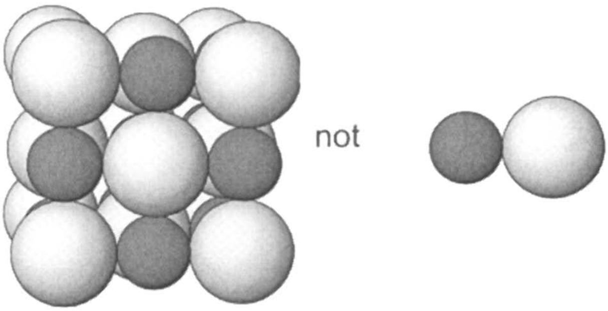

Figure 2. Ion packing in the structure of NaCl

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chloride anion is surrounded by six sodium cations. Numerous investigators have probed the structure of liquid NaCl, and it is generally concluded that a similar structural organization exists in the liquid state (*2*). Thus, while an ionic liquid is a polarizable medium it is not anticipated to be a polar liquid unless either the anion or cation itself is polar. Of course a strong dipole in either the anion or cation is likely to increase the melting temperature of a salt.

The crystal structures of [EMIM][PF_6] and [C_{12}MIM][PF_6] (C_{12}MIM = 1-dodecyl-3-methylimidazolium) have recently been reported (*6,10*), and they demonstrate that the organization in these complex salts is analogous to that observed in NaCl. The non-standard unit cell of the [EMIM][PF_6] salt, shown in Figure 3 viewed perpendicular to the (1 0 -2) plane, demonstrates the NaCl-type packing arrangement that is observed in this salt. Five reasonably short contacts are observed between the imidazolium cation and neighboring PF_6 anions (C-P or N-P contacts of less than 4.5Å) with a sixth contact (of about 6Å) that has been lengthened by the ethyl group bound to the imidazole ring. Similarly six imidazolium cations surround each PF_6 anion in a distorted octahedral fashion. The close points of contact between the imidazolium cation and the PF_6 anion are the aromatic protons and the nitrogen atoms consistent with the charge distribution described in the previous section (although the alkyl CH protons are also in close proximity to the anions). The methyl and ethyl groups are oriented in alternating directions so as to give the most efficient packing while beginning to separate the charged and neutral portions of the imidazolium cation. When the neutral portion of the imidazolium cation is increased to the size of a $CH_3(CH_2)_{11}$ chain more dramatic phase separation between the neutral and charged portions of the lattice is observed resulting in a lamellar bi-layer type

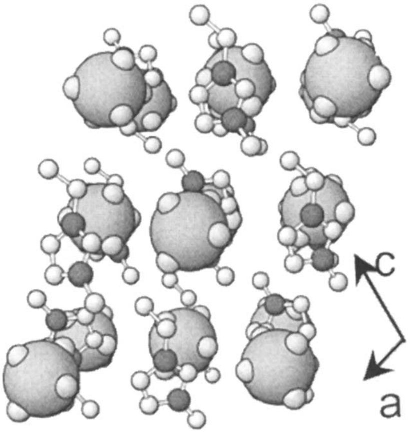

Figure 3: Crystal Structure of [EMIM][PF_6] illustrating the NaCl-Type packing

organization as seen in Figure 4. Nevertheless, examination of the interaction between the cationic heads of the $[C_{12}MIM]^+$ and the $[PF_6]^-$ anions finds an analogous sodium chloride-type organization. Here each $[PF_6]^-$ anion is surrounded by five imidazolium cations and each imidazolium cation is surrounded with five $[PF_6]^-$ anions (anions (C-P or N-P contacts of less than 4.5Å), consistent with a two layer slice of the NaCl-type lattice. Thus, the bulk structural organization consists of two alternating non-polar regions, the salt-like packing of anions and cationic heads, and the hydrocarbon-like regions of the alkyl tails.

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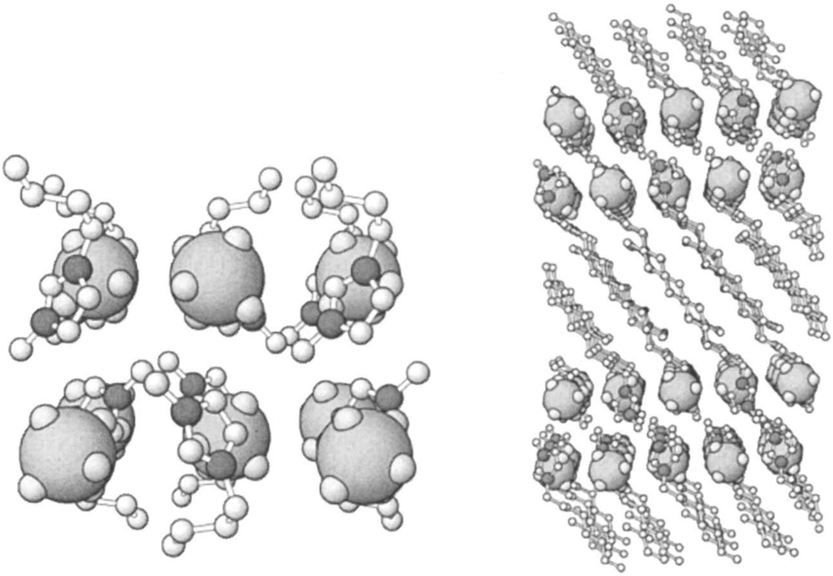

Figure 4. Structure of $[C_{12}MIM]PF_6$ emphasizing the NaCl-type packing within the cationic head/anion region and the phase separation of the ionic and hydrocarbon regions in the bulk crystal. (The alkyl chains are truncated in 4a.)

Although the electrostatic interaction of the cations and anions require a non-polar structural organization, polar characteristics of an ionic liquid can be realized for materials with polar cations or anions. For example, the observed polarity of several [EMIM][X] ionic liquids, which have been compared with CH_3CN or low alcohols (*11*), may originate from the asymmetric charge distribution in the imidazolium cation in which the C2 hydrogen is significantly more acidic than the C4 and C5 protons (*5*). The polarity of this cation is somewhat unusual in that the distribution of positive charge creates the dipole as opposed to a dipole resulting from an increased electron density on an electronegative atom. This contrasting origin of the dipole makes $[EMIM]^+$ a polar, but generally non-coordinating species. From a similar consideration of the geometry of the anion, it would be expected that nitrite salts, $[NO_2]^-$, will form more polar solvents than nitrate, $[NO_3]^-$, salts. However, the solubility characteristics of a polar ionic liquid and a polar molecular solvent are expected to be notably different because of the energetic cost of charge separation associated with solvation. In an ionic liquid, ions must be separated from the network of charge compensating counter ions to form a solvation shell around the solute. The electrostatic competition for a polar ion to interact with its counter ion or a solute will tend to reduce solubility in ionic liquids as compared to neutral polar solvents in which the respective dipole moments of the polar ions and molecules are of a similar magnitude.

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Crystalline vs. Liquid Structures

What then are the relationships between the crystalline structures described above and their structures in the liquid phase? Understanding the structure of liquids at an atomic or molecular level of organization is quite challenging and has been the subject of considerable investigation and controversy; with most significant early advances coincident with the development of X-ray and Neutron scattering techniques (*12*). Watching children "swim" through a pool of plastic spheres in a playground "ball-pen" leads one to believe that this may be a quite reasonable macroscopic model of the structural organization in liquids. Similar plastic spheres when ordered into a periodic lattice provide a macroscopic model of many crystalline structures as well. The difference between the organization of balls in the playground pool or in a model of a crystalline lattice of NaCl is minimal. Both exhibit an approximately close-packed arrangement of spheres. These structural observations led us to think about the structure of liquids from a starting point of a crystalline model, albeit with the break down of long range order.

The neutron scattering pattern for liquid NaCl at 820 °C is shown in Figure 5 (*2b*). Such measurements have been made and analyzed by a number of authors, and the general conclusion is that in liquid the Na-Cl distance is about 2.78Å and the Cl-Cl distance is about 3.91Å. These values are quite similar to those of crystalline NaCl at high temperature just prior to melting (*2*). It has further been noted that the strong scattering features in the S_{QQ} (the charge density structure factor, which describes the charge ordering of the anions and cations) (Figure 5a) occur at values of Q (the reciprocal space wave vector, $Q = (4\pi \sin \theta)/\lambda)$) which reasonably correspond to the position of the first Bragg reflections of the crystalline material (Figure 5d) (*2b*). When we ignore the periodic lattice conditions for crystalline diffraction and calculate the expected scattering for an NaCl-type structure in which the scattering originates from atom atom contacts within a 5Å radius, the pattern shown in Figure 5c is obtained (*13*) which shows definite similarity to the measured S_{NN} (the number density structure factor) of Figure 5b. These data suggest that the charge ordering may have a longer coherence length than the atom ordering. And while long range order is lost on going from the crystal to the liquid, similarities in structure remain as a consequence of the coulombic forces between anions and cations.

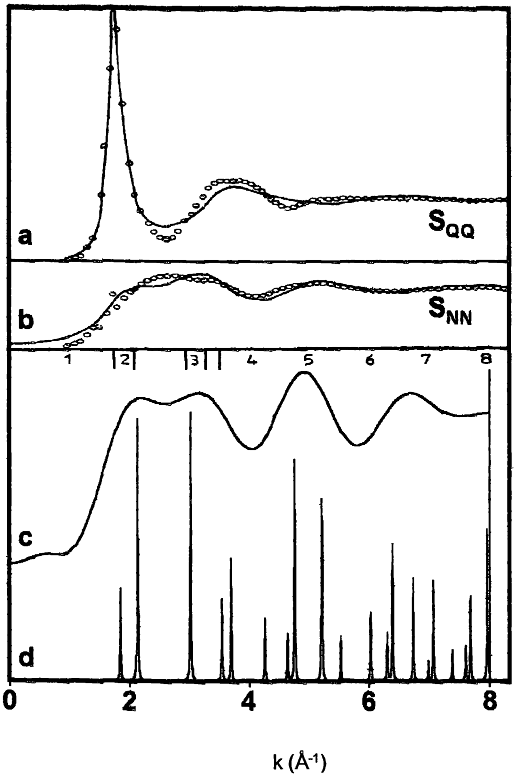

Figure 5. (a, b) Bhatia-Thornton structure factors S_{QQ} and S_{NN} for molten NaCl (reproduced with permission from refrence 2b, © 1986, Institute of Physics Publishing). (c) Simulated neutron scattering for liquid NaCl using a 5Å coherence length. (d) Calculated neutron diffraction for crystalline NaCl.

Liquid crystals represent the class of liquids for which the most dramatic structural organization is observed in the liquid phase. When the coherence length of the molecular organization is greater than the wavelengths of

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visible light, birefringence patterns are observed. Control over the direction of structural organization is the basis for the widely used liquid crystal display technology. We and others have noted that liquid crystalline ionic liquids can frequently be formed by attaching an alkyl tail with a chain length greater than 10 carbons to either the anion or cation (*9,10,14*). The variable temperature synchrotron X-ray diffraction of C_{16}TA-ZnCl-33 ([cetyltrimethylammonium]$_2$ [$ZnCl_4$]), shown in Figure 6, clearly demonstrates the similarity between the crystalline and liquid crystalline structures (*9*). The crystalline structure consists of an A_2X salt-like organization of cationic trimethylammonium head groups and $[ZnCl_4]^{2-}$ anions, which are separated by interdigitated surfactant tails resulting in the overall lamellar structure. The relative charge density of the anion and trimethyammonium head require that the surfactant tails be canted with respect to the salt-type layer in the crystalline phase in order to maintain van der Waals contacts between the surfactant tails. This results in lamellar d-spacing significantly less than the length of the surfactant. (The structure of C_{16}TA-ZnCl-33 is similar to the structure of [C_{12}MIM][PF_6] shown in Figure 4.) Upon melting to the first lamellar liquid crystalline phase at about 70 °C, an increase in the lamellar spacing of about 1Å is observed, seen by the shift to lower angle diffraction, as the van der Waals interactions between hydrocarbon chains are relaxed upon chain 'melting.' Nevertheless, the diffraction indicates that

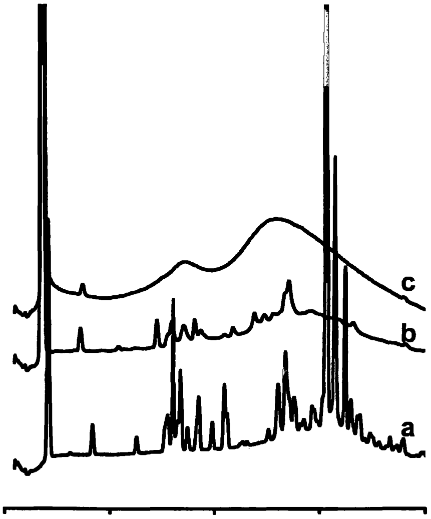

Figure 6. Synchrotron XRD of C_{16}TA-ZnCl-33. (a) Crystalline material at room temperature. (b) L_1 liquid crystal at 90 °C. (c) L_2 liquid crystal at 200 °C.

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significant lateral organization remains in addition to the lamellar organization in this S_C-type liquid crystal. A liquid-liquid phase transition occurs upon further heating to about 160 °C at which point the long-range lateral organization in the liquid is lost, but sharp diffraction resulting from the lamellar ordering, Q ~ 0.2Å^{-1}, 0.4Å^{-1}, and 0.6Å, remains. Nevertheless, while the sharp diffraction originating from long-range lateral order in the crystal is lost, it is replaced by broad features in the scattering pattern in this S_A-type liquid crystal. These broad features are indicative of the retention of intermediate range order, which had its origins from the long-range order of the crystalline organization.

Metallotropism and the Structure of Liquids

Finally in our consideration of structure in ionic liquids it is important to understand how composition and cation charge density impact the observed structure of the anions; a concept we describe as *metallotropism*. The relationship between composition and anion structure to properties such as the melting point was noted above in the complex phase diagrams. For example, metal halide materials can exhibit compositions ranging from the isolated anion $[X]^{n-}$ to the neutral composition of the MX_n parent. The structural preferences of the metal, M, (i.e. oxidation state, coordination geometry and etc.) provide the ground rules for anion oligomerization. But the nature of the oligomers formed reflect a balance of the charge density constraints of the inorganic anion and the templating cation, as represented in Scheme I. Without a readily avalible means to determine the structures of the liquid phase anions, we turn to a consideration of crystalline structures to understand these charge density influences on anion structure, which, as discussed above, provide a reasonable starting model for understanding the structure of liquids.

		Inorganic Charge Density	
Template Charge Density		High	Low
	High	low-dimensional networks and chains	3-D networks
	Low	molecular anions	low-dimensional networks and chains

SCHEME I. Charge Density vs. Network Oligomerizaion

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Consider the *metallotropism* in the zinc chloride system as an example (Figure 7). In the binary system $ACl/ZnCl_2$ (A = monopositive cation), the maximal inorganic charge density will be found on the $[X]^-$ rich side of the phase diagram, whereas, low charge density species are found toward the $ZnCl_2$ rich compositions. Zn^{2+} prefers a tetrahedral coordination by halides, and the parent anhydrous phase δ-$ZnCl_2$ exhibits a 3-D network of corner-sharing tetrahedra (15). The most chloride rich composition reported is at 20 mole % $ZnCl_2$ corresponding to the composition $[ZnCl_6]^{4-}$ (*8*). While an octahedral geometry might be presumed, we have not yet found crystallographic evidence for this anion. At 33 %, the tetrahedral anion $[ZnCl_4]^{2-}$ is observed with a variety of cations. At 50% we have characterized the structure of the $[Zn_2Cl_6]^{2-}$ which adopts an edge-shared tetrahedral dimer geometry in the crystal structure of $[C_{16}TA]_2Zn_2Cl_6$ (*16*), however in the liquid crystalline state we have evidence suggesting that the corner-shared tetrahedral polymer $[ZnCl]^-_\infty$ exists.

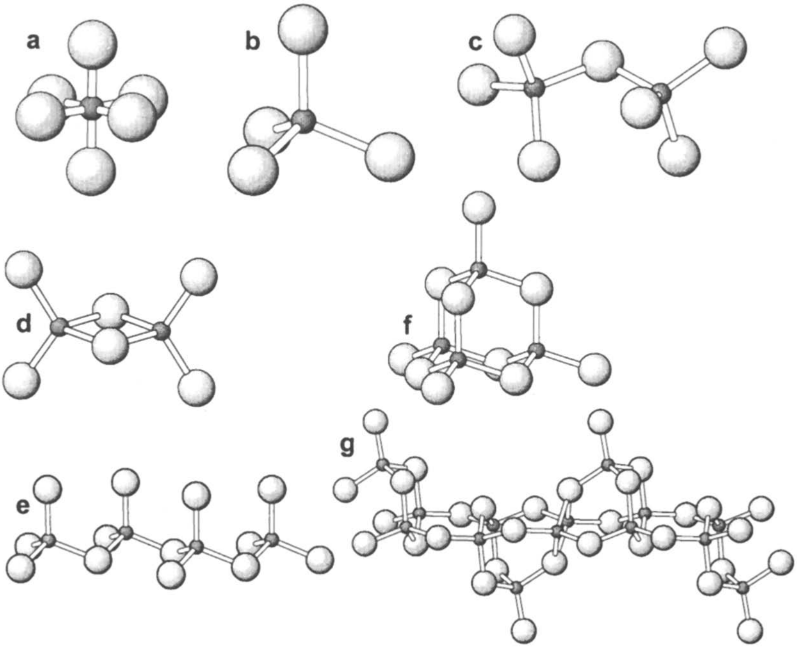

*Figure 7. Composition dependent metallotropism of zinc chloride. (a) 20%-"$[ZnCl_6]^-$", (b) 33%-$[ZnCl_4]^{2-}$, (c) 40%-"$[Zn_2Cl_7]^{3-}$", (d) 50%-$[Zn_2Cl_6]^{2-}$ (*16*), (e) 50%-"$[ZnCl_3]^-$", (f) 66%-$[Zn_4Cl_{10}]^{2-}$ (*17*), (g) 75%-$[Zn_6Cl_{14}]^{2-}$ (*18*).*

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At the 66% composition the $[Zn_4Cl_{10}]^{2-}$ anion has been observed (*17*) and the polymeric $[Zn_6Cl_{14}]^{2-}{}_{\infty}$ is observed at 75% zinc chloride (*18*). The complex anions described represent the progression from left to right across the inorganic charge density axis in Scheme I.

Alternatively one must also consider the *metallotropism* directed by the charge density of the counter cation. We recently described the template dependence of structure in the cuprous chloride system (*19*). Keeping the inorganic charge density compositionally constant in the $[A]CuCl_2$ salts (two cuprousbromide salts (*20, 21*) are also considered here), considerable structural variation is observed as shown in Figure 8: from the linear $[CuCl_2]^-$ molecular anion found for low charge density cations such as tetrapropyl ammonium, $[NPr_4]^+$ (*22*), to the recently reported 2-D network of $[CuBr_2]^-$ templated by the small ammonium head group of $[4,6\text{-}Br_2\text{-}3\text{-}Cl\text{-anilinium}]^+$ (*21*). The complex anions described from Figure 8a to 8e (*19-23*) represent a progression from the bottom to the top of the template charge density axis in Scheme I.

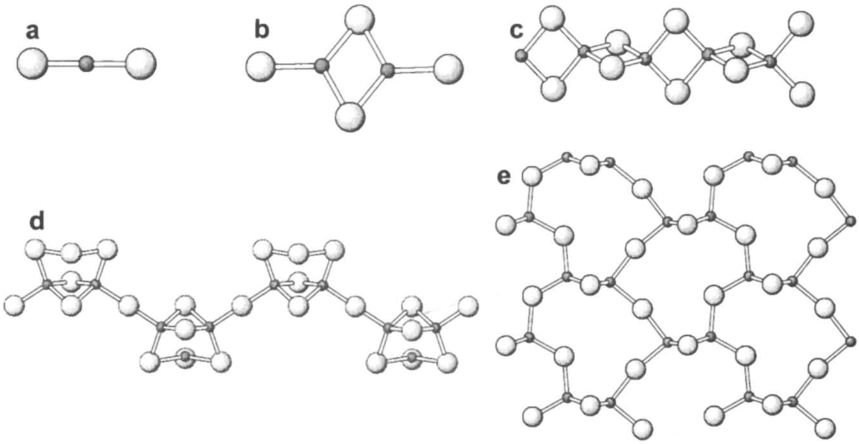

Figure 8. Counter cation induced metallotropism in $[CuCl_2]^-{}_n$ anions. (a) $[CuCl_2]^-$ (22), (b) $[Cu_2Cl_4]^{2-}$ (20), (c) $[CuCl_2]^-{}_{\infty}$ (23), (d) $[Cu_3Cl_6]^{3-}$ (19), (e) $[CuCl_2]^-{}_{\infty\infty}$ (21).

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It is unlikely that all the complex structures shown in Figures 7 and 8 are retained upon melting into the liquid state (although many of these copper and zinc salts exhibit melting points below 150 °C). Nevertheless, the principles of metallotropism are independent of whether the material is in a crystalline or liquid state. Furthermore, it is clear that a greater variation in structure of the complex anions is to be expected in the inorganic rich side of the phase diagram (traditionally referred to as acidic melts).

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Conclusions

Like all materials, the structure and properties of ionic liquids are intimately related. While structural organization beyond the local order of the constituent ions is much less in a liquid than in a crystal, the extended structural organization of a crystalline lattice provides a reasonable starting point for understanding structural features in the liquid state. The size, shape, and distribution of charge in the respective ions determines the magnitude of the inter-ionic interactions. With a large size and low charge density, the coulombic attraction between ions is reduced to the order of magnitude of intermolecular interactions in molecular liquids such that low temperature ionic liquids can be formed. However, in the liquid state, as in the solid state, the anions and cations will be organized so as to neutralize charge in the bulk material. This salt-type packing of ions will result in a non-polar, but polarizable medium. Finally, the structural diversity among $[M_nX_m]^{x-}$ anions is articulated as a compositional- or counter cation directed-metallotropism. The former includes the compositional fine tuning of the anionic charge density across the $AX/[MX_m]$ phase diagram, whereas the latter articulates the impact of the charge density of the cation $[A]^+$ on the structure of the anion $[M_nX_m]^{x-}$. Understanding the role of size, shape and charge density thus allows for the possibility to design ionic liquids with tailored structures and properties.

Acknowledgements

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Chapter 33

Photochemistry in Ionic Liquids

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This chapter describes our and other researchers' investigations into photochemistry in ionic liquids. The first part will describe our investigations into the nature of ionic liquids as solvents. The remainder of the chapter will describe our investigations into how ionic liquids can influence some fundamental reaction types.

Ionic liquids have attracted great interest in recent years as alternative reaction media to supplement or replace conventional organic solvents (*1-3*). This work has been driven in part by the idea that ionic liquids represent a "greener" alternative to such media, largely as a result of their negligible vapour pressures, resulting in greatly improved control over harmful emissions. Increasingly, however, the interest has arisen from the fact that ionic liquids can provide real improvements in performance over conventional systems.

One area that has received little attention to date, however, is photochemistry in ionic liquids. This may be explained by the fact that many examples of synthetic photochemistry require relatively dilute reaction solutions,

In Ionic Liquids; Rogers, R., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2002.

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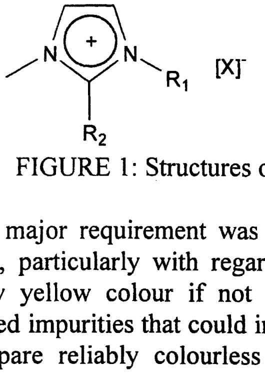
and hence quite large volumes of solvent. Nevertheless, photochemical reactions often result in different product distributions from those obtained in thermal reactions, and in some cases can provide access to alternative reaction products. Furthermore, the use of techniques such as laser flash photolysis has been instrumental in the determination of reaction mechanisms. Such information has provided important information regarding the nature of many reactive intermediates, and thus enhanced the understanding of many chemical processes. Equally neglected have been photophysical investigations involving ionic liquids. Many different probe molecules can provide important information about the manner in which a reaction medium will interact with different types of solute molecule. This chapter will describe efforts by us and other researchers to remedy this gap in the understanding of ionic liquids.

The work described here will be largely confined to ionic liquids based on 1-alkyl-3-methylimidazolium cations ([Rmim]$^+$). This is not due to any property inherent in such salts, but simply because [Rmim]$^+$ salts have dominated the literature over the past ten years or so. As other types of ionic liquid become more commonly used, we hope to be able to expand the scope of our investigations. The main liquids employed are illustrated in Figure 1 along with the abbreviations used to identify particular cations or anions.



$R_1 = C_4H_9$, $R_2 = H$: [bmim]$^+$
$R_1 = C_4H_9$, $R_2 = CH_3$: [bmmim]$^+$
$R_1 = C_8H_{17}$, $R_2 = H$: [omim]$^+$
$R_1 = C_8H_{17}$, $R_2 = CH_3$: [ommim]$^+$
$X = PF_6$, BF_4, CF_3SO_3 (TfO), $(CF_3SO_2)_2N$ (Tf_2N)

FIGURE 1: Structures of ionic liquids employed in these studies

A major requirement was the preparation of "spectroscopic grade" ionic liquids, particularly with regard to their colour. Many ionic liquids have a slightly yellow colour if not carefully prepared, indicating the presence of coloured impurities that could interfere with the processes under study. In order to prepare reliably colourless ionic liquids, a number of precautions were required which are outlined in the experimental section at the end of this chapter. The photochemical window of such liquids is quite wide, with effectively no absorbance at $\lambda > 300$ nm in "clean" liquids.

A study of the literature reveals only three papers describing photochemistry in room temperature ionic liquids of this type. The first report, by Osteryoung and co-workers (*4*), describes the photooxidation of iron(II) diimine complexes in acidic ionic liquids based on the 1-ethylpyridinium bromide/aluminium(III) chloride system. These reactions gave almost quantitative formation of iron(III) diimine complexes. It was suggested that the ethylpyridinium cation was acting as the electron acceptor, and that the radical species thus formed then dimerised to form a highly coloured species displaying a new absorption band at 680 nm.

More recently, Pagni and co-workers (*5*, *6*) described the photoreactions of anthracene (An) and 9-methylanthracene ($9\text{-}CH_3An$) in 1-ethyl-3-methylimidazolium (emim) and 1-butylpyridinium (bp)/ aluminium(III) chloride ionic liquids. Both acidic and basic systems were investigated, giving different results. Irradiation of An in basic emim-based ionic liquids gave exclusively the 4+4 dimer formed in conventional solvents like CH_3CN. Irradiation of $9\text{-}CH_3An$ on the other hand yielded the dimer as the major product, but also six minor products not observed in conventional solvents. These results suggested that 20% of the photoreaction in the ionic liquid occurred *via* pathways initiated by electron transfer from excited state $9\text{-}CH_3An$ to the solvent cation. A somewhat different product mixture was formed in the bp-based melts, an observation that was ascribed to the greater ease of reduction of $[bp]^+$ than $[emim]^+$. It was also noted that reactions involving bimolecular processes occurred more slowly in the ionic liquids than in the less viscous CH_3CN. Overall, it appears that photochemical reactions can follow different pathways in ionic liquids and conventional solvents. The evidence suggests that the imidazolium and pyridinium cations can act as electron acceptors.

Solvent Properties Of Ionic Liquids

There have now been many reports of the use of ionic liquids for a wide range of chemical applications (*1-3*). In contrast however, there are remarkably little physical data reporting their solvent properties. The ground and excited states of many molecules are strongly influenced by interactions with their environment. For this reason, the photophysical behaviour of appropriate probe molecules can be used to investigate the manner in which solvents interact with different solutes. Such information is extremely important if reactivity patterns are to be understood, and until recently there has been a dearth of such information for ionic liquids. One complicating factor is the chemical complexity of the liquids themselves. Clearly, a mixture of cations and anions potentially doubles the number of different interactions that must be considered. A wide range of photophysical probes now exist, but most only probe particular interactions with solvent molecules. The probes used must be chosen with care, therefore, before a "polarity" scale for ionic liquids may be prepared.

Although a number of authors have reported the use of solvatochromic probe molecules to investigate the behaviour of molten salts based on alkylammonium cations, only a handful of such studies are reported for $[R\text{-}mim]^+$ based salts. Bonhôte *et al.* showed that $[emim][Tf_2N]$ displayed a polarity similar to that of ethanol based on the fluorescence spectrum of pyrene

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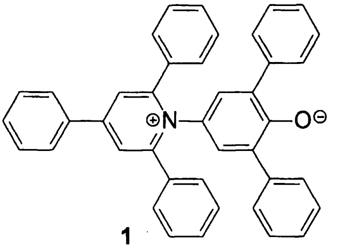
(*7*). They also reported that the apparent relative permittivity value for this solvent was below 10, based on the fluorescence spectrum of pyrenecarboxaldehyde. Finally, room temperature phosphorescence of 1-bromonaphthalene was observed in this solvent. More recently, Carmichael and Seddon reported a study of the UV-visible absorption spectrum of the solvatochromic dye Nile Red in a range of $[Rmim]^+$ based salts showing similar λ_{max} values to those obtained in short chain alcohols (*8*). Alteration of the length of the alkyl substituent had little effect on the position of λ_{max}. Finally, Brennecke co-workers have investigated the polarity of four $[Rmim]^+$ and pyridinium based salts using the fluorescent probes 4-aminophthalimide and 4-(*N,N*-dimethylamino)phthalimide (*9*). Their data indicated polarities lying between those of methanol and acetonitrile, depending on the cation present.

Reichardt's dye

One of the most widely used polarity scales is the E_T scale, first reported by Reichardt based on the betaine dye **1** (commonly know as Reichardt's dye) (*10*, *11*).



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This molecule displays a strong intramolecular charge-transfer absorption that is shifted by over 350 nm on moving from non-polar solvents such as diphenyl ether (λ_{max} = 810 nm) to polar solvents such as water (λ_{max} = 453 nm). The large negative solvatochromism arises from a difference in solvation of the electronic ground and excited states. Taft and Kamlet calculated that *ca.* 68% of the shift in transition energy could be assigned directly to a hydrogen bonding interaction with O^- (*12*), thus indicating that the E_T scale is largely a measure of hydrogen bond donor strength for protic solvents. Compound **1** has been previously applied to investigations of a number of non-imidazolium based molten salts (*13-16*).

We recorded the UV-visible spectrum of **1** in a range of imidazolium-based ionic liquids, investigating the effect of alteration of both the cation and anion (*17*). The values obtained are listed in Table I, along with some previously reported molten salt values, and some for conventional molecular solvents. The

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values $E_T(30)$ and E_T^N are parameters calculated from the value of λ_{max}, representing the molar transition energy and a normalised polarity scale respectively. The limits of the E_T^N scale are water (E_T^N = 1.0) and tetramethylsilane, TMS (E_T^N = 0.0) (*10, 11*).

Table I. λ_{max}, $E_T(30)$ and E_T^N values observed for 1, and λ_{max} values observed for 2 in a range of ionic liquids and other solvents at 298 K

Solvent	λ_{max} (1) / nm	$E_T(30)$ / kcal mol^{-1}	E_T^N	λ_{max} (2) / nm
Imidazolium-based ionic liquids				
[bmim][PF_6]	546.5	52.3	0.667	516.5
[omim][PF_6]	558.0	51.2	0.633	516.5
[bmim][Tf_2N]	555.5	51.5	0.642	546.0
[omim][Tf_2N]	559.0	51.1	0.629	548.5
[bmmim][Tf_2N]	588.0	48.6	0.552	547.5
[ommim][Tf_2N]	599.5	47.7	0.525	549.5
[bmim][TfO]	547.0	52.3	0.667	601.5
[bmim][BF_4]	545.0	52.5	0.673	-
[ommim][BF_4]	592.0	48.3	0.543	-
Other molten salts (11)				
[$C_2H_5NH_3$][NO_3]	464	61.6	0.954	-
[$(C_4H_9)_3NH$][NO_3]	504	56.7	0.803	-
[$(C_6H_{13})_4N$][$C_6H_5CO_2$]	651	43.9	0.407	-
"Conventional" solvents (11)				
Ethanol	551	51.9	0.654	585
Propan-2-ol	591	48.4	0.546	591
1,2-Dichloroethane	692	41.3	0.327	500
Acetone	678	42.2	0.355	569
N,N-Dimethylformamide	662	43.2	0.386	602

The data for the imidazolium salts fall into two distinct categories: the 1,3-disubstituted cations give $E_T(30)$ values close to those obtained for short chain primary alcohols, while the 1,2,3-trisubstituted cations had noticeably lower E_T values, similar to those obtained for secondary alcohols. Thus, the methyl group at the 2-position on the imidazolium ring clearly results in weaker interactions with **1**. These results suggest that the strongest influence on the value of $E_T(30)$ is the strength of the hydrogen bonding interaction between the imidazolium ring protons and the phenoxide oxygen on **1**. Alteration of the anion seems to have little effect on the E_T values for a particular cation, although [bmim][Tf_2N]

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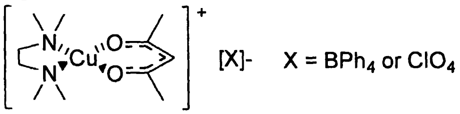
displays a λ_{max} value approximately 10 nm higher than that observed for other salts containing the $[bmim]^+$ cation. The reason for this anomalous value is not currently understood. An increase in the length of one of the *N*-alkyl substituents results in only modest decrease in the E_T value. This concurs with observations made using the same probe molecule for primary alcohols of varying alkyl chain length, where increasing chain length was found to give a similar effect to that observed on addition of *n*-hexane to short chain alcohols (*18*). The non-imidazolium ionic liquids straddle our values; those containing acidic protons (*i.e.* ammonium salts) possess high E_T values, and those without (*i.e.*, tetraalkylammonium salts) lower.

When carrying out polarity measurements, two *caveats* must be highlighted. Although the $[PF_6]^-$ and $[Tf_2N]^-$ based ionic liquids reported here are hydrophobic, this does not mean that they are entirely water free, unless specifically pre-dried. Even small quantities of water can have a significant effect on the position of λ_{max} of **1**. For example, in water saturated $[bmim][PF_6]$ λ_{max} = 526 nm, compared with a value of 546.5 nm in the dry liquid at 298 K. Thus, care must be taken to ensure that the liquids are dry when novel values are reported. The measurements reported in Table I were recorded using liquids containing **1** which were heated under vacuum at 70 °C until no further red shift in the CT band was observed. Despite these precautions, it is possible that traces of water remain, but we believe that these values are as accurate as may be obtained under the conditions generally employed for drying ionic liquids. Similarly, the presence of even small traces of other solvents of different polarities can also cause large changes in the position of λ_{max}. A second potential problem can arise either in ionic liquids that are prepared from free acids, or in ones in which the formation of a protic acid might occur *via* decomposition. The presence of any significant quantity of free H^+ ions can result in protonation of **1** at the oxygen atom, yielding a colourless species which is useless as a measure of relative polarity.

Basicity of ionic liquids

The results listed above clearly suggest that the imidazolium-based ionic liquids can act as H-bond donor solvents, and that the strength of the interaction is largely cation dependent. We have used the Cu^{2+} salt **2** to probe the basicity of a range of ionic liquids.



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It has previously been shown that there is a correlation between the position of the lowest energy d-d band of this salt and the donor number of a solvent (*19-21*). More recently, the same salt has been used to estimate the donor number of anions in solution (*22*). The solvatochromism arises from changes in the splitting of the d-orbitals of Cu^{2+} as the salt becomes five- or six-coordinated. The probe is used as a $[BPh_4]^-$ salt as this anion is assumed to be entirely non-coordinating. The λ_{max} values obtained for **2** in a range of ionic liquids are listed in Table I, along with those for some conventional solvents.

The data clearly show that the basicity of the ionic liquids employed here is entirely anion dependent, the order being $[PF_6]^- < [Tf_2N]^- < [TfO]^-$. Unfortunately, no consistent results could be obtained for $[BF_4]^-$ salts. Based on previous data one would expect the value to lie between that of $[PF_6]^-$ and $[Tf_2N]^-$, whereas different values in the range 550-600 nm were generally observed. We ascribe this to the presence of traces of Cl^- or Br^- in the water miscible $[BF_4]^-$ salts. The polarity data from **1** and **2** have recently been used to provide an explanation for the rate enhancements often observed when ionic liquids are used as solvents for biphasic catalysis (23).

Laser flash photolysis investigations in ionic liquids

Laser flash photolysis is an extremely versatile technique for investigating the behaviour of reactive intermediates. Photochemical processes may be studied by following the time dependence of either absorbance spectra or luminescence. We have applied laser flash photolysis with UV-visible detection to three different photochemical systems, notably benzophenone, $[Ru(bpy)_3]^{2+}$ and Diels-Alder reactions of $^1O_2$. The first of these will be described in some detail, and results gained will be related to the other systems where appropriate.

One of the most widely studied areas of photochemistry involves that of benzophenone and other organic ketones. One of the "classic" systems of this type is the benzophenone/naphthalene (or naphthalene derivative) couple, whose behaviour has been investigated in a wide range of different solvents (*24*). The first step of this process involves the photoexcitation of benzophenone (Bp), ultimately giving the $n\pi^*$ triplet excited state $^3Bp^*$. In this lowest excited state, the C=O bond is considerably weakened compared with the ground state, which means that $^3Bp^*$ can also be considered as a biradical species, as indicated in Scheme 1 below (*25*). This species can then undergo a number of deactivation processes, the most important of which are phosphorescence, quenching *via* triplet energy transfer to an appropriate quencher (**Q**, *e.g.* naphthalene), or hydrogen atom abstraction from the solvent to form a ketyl radical (KR). The degree of quenching is dependent on the concentration of naphthalene present, while the contribution of hydrogen abstraction is solvent-dependent.

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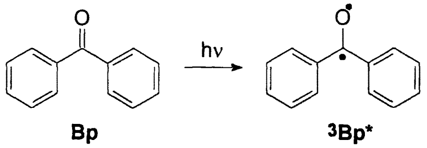

$^3Bp^* \xrightarrow{h\nu'} Bp$ Phosphorescence

$^3Bp^* + Q \longrightarrow Bp + Q$ Quenching

$^3Bp^* + RH \longrightarrow KR + R\bullet$ H abstraction

Scheme 1

Hydrogen abstraction

We have investigated both the H-abstraction reaction and the quenching reaction with naphthalene in five different ionic liquids as well as a number of conventional organic solvents for comparison (*26*). Flash photolytic excitation (λ_{ex} = 355nm) of 5 mM solutions of Bp in the ionic liquids gave rise to a broad feature with a maximum around λ = 525 nm in all cases. This species decayed over several microseconds forming a second, long-lived species that exhibited a slight solvent dependence in its absorption maximum (λ_{max} = 530-550 nm). An example of the spectra obtained is shown in Figure 2.

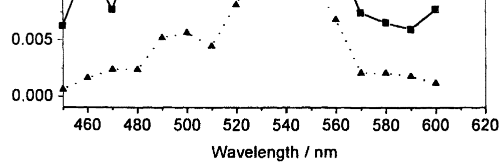

Figure 2. Transient spectra at 23.5 °C of ^{3}Bp* and KR in [omim][Tf$_2$N], λ_{ex} = 355 nm. The spectra are recorded 0.2 μs (squares, solid line) and 16.0 μs (triangles, dotted line) after the laser pulse. The inset shows a typical kinetic trace recorded at λ = 530 nm.

The initially formed, short–lived, component was quenched by naphthalene at a diffusion controlled rate, forming triplet excited state naphthalene (λ_{max} = 425 nm). The decay rate of both components was strongly dependent on oxygen concentration. We are therefore very confident of the assignment of the short-lived species as ^{3}Bp*. KR is known to exhibit a λ_{max} value around 540 nm (+/-10 nm), depending on the solvent (*27*). The long-lived component absorbing >15 μs after the laser pulse is therefore fully consistent with the presence of this species. In the ionic liquids, the yield of the long-lived species increased with increasing temperature, indicating an increasing quantum yield for the H-abstraction process. In cyclohexane, 1-butanol and toluene, on the other hand, little change was observed over the temperature range investigated.

In the absence of Np, the rate constant for the decay of ^{3}Bp* (k_{obs}) is given by the equation:

$$k_{obs} = k_H + k_T$$

where k_H is the rate constant for the hydrogen abstraction process, and k_T the rate constant for deactivation *via* intersystem crossing. Based on the assumption that the absorbance measured directly after the laser pulse arises entirely from ^{3}Bp*, while the absorbance after several μs arises from KR only, it is possible to calculate the values of k_H and k_T from the intensities of the transient absorption bands for ^{3}Bp* and KR. Using the values of k_H recorded at a range of temperatures, the Arrhenius parameters listed in Table II were obtained for a range of ionic liquids, along with some conventional solvents in which hydrogen abstraction is also observed. The calculations assumed that the ratio of molar extinction coefficients for ^{3}Bp* and KR at 530 nm was 2.4, based on the assumption that all ^{3}Bp* was converted to KR at high temperatures in the [omim]$^+$ salts. Clearly, this value may not hold for all ionic liquids, but the value of E_a^H is unaffected by this ratio, only the value of the pre-exponential factor A_H, which must therefore be assumed to contain relatively large errors.

Table II. Arrhenius parameters obtained for H-abstraction by ^{3}Bp* from a range of ionic liquids and organic solvents

Solvent	k_{obs} / s^{-1} [a]	k_H / s^{-1} [a]	A_H / s^{-1}	E_a^H / kJmol^{-1}
[bmim][PF$_6$]	3.6 x 10^5	2.0 x 10^5	5.9 x 10^9	25.4
[omim][PF$_6$]	4.8 x 10^5	3.4 x 10^5	2.7 x 10^9	22.2
[bmim][Tf$_2$N]	3.2 x 10^5	1.4 x 10^5	9.8 x 10^8	21.9
[bmmim][Tf$_2$N]	7.3 x 10^5	1.7 x 10^5	1.1 x 10^{10}	27.3
[omim][Tf$_2$N]	1.3 x 10^6	7.3 x 10^5	4.8 x 10^9	21.6
Toluene	3.0 x 10^6	3.0 x 10^6	9.8 x 10^8	14.5
Cyclohexane	4.9 x 10^6	4.9 x 10^6	1.3 x 10^9	13.7
1-Butanol	1.1 x 10^7	1.1 x 10^7	2.4 x 10^9	13.3

[a] At 23.5 °C

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It is clear from Table II that:

- the activation energy for hydrogen abstraction is effectively identical in all ionic liquids investigated, and *ca.* 10 kJ mol^{-1} higher than that observed in the conventional solvents and,
- the rate constant k_H for hydrogen abstraction is an order of magnitude lower in the ionic liquids than in the conventional solvents.

The fact that the rate of abstraction increases with increasing alkyl chain length, along with an increase in the pre-exponential factor A, suggests that only the C-H bonds of the alkyl substituents are being broken. The reason for the lower degree of hydrogen abstraction observed in the ionic liquids is currently not clear. One obvious suggestion is that there is a specific interaction between the benzophenone carbonyl group and the hydrogen atoms on the imidazolium ring, resulting in a stabilisation of the ground state. This would be expected to result in shifts in the position of the nπ* transition in the UV-visible spectrum. In fact, the UV-visible spectrum of Bp in all of the ionic liquids is effectively identical, with the λ_{max} of the nπ* absorption lying around 338 nm, between that observed for methanol and acetonitrile. Unfortunately the ππ* transition cannot be observed owing to the absorption of the solvent, but the position of the solvent edge suggests no significant shift compared with other solvents. Another possibility is that the C-H bonds in the ionic liquids are stronger than in the conventional organic solvents. The fact that the ν(CH) regions in the infrared spectra of the ionic liquids are very similar to those observed for conventional alkyl groups would argue that this is also not the case, however.

Thus we are left only with the possibility that interactions are occurring in the excited state that do not occur in the conventional solvents. It is possible that the dipole of Bp means that it is preferentially solvated by the dipolar imidazolium headgroup of the cation, and thus that the hydrogen abstraction reaction requires a large change in geometry. We currently have no spectroscopic or other information to support this hypothesis however. Nonetheless, it is clear that the ionic liquids are more resistant to radical abstraction reactions than many conventional media, and may suggest that such reactions might be carried out efficiently in these solvents. There is already evidence that ionic liquids represent excellent media in which to carry out radical polymerisation reactions (*28*).

Bimolecular processes in ionic liquids

The rate of quenching of the phosphorescence of $^3Bp^*$ by Np (k_{obs}) was recorded over a range of temperatures and concentrations of Np, for each of the ionic liquids. A plot of k_{obs} *vs.* [Np] allowed the calculation of a value for the bimolecular rate constant (k_q) for the quenching reaction at each of the

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temperatures under study, which in turn allowed the construction of Arrhenius plots for each solvent. Using these plots it was possible to calculate the activation energy for the bimolecular triplet energy transfer reaction (E_a^R), and the entropy of activation $\Delta S^\ddagger$. The activation energies for viscous flow (E_a^V) for all of the ionic liquids under study were also calculated using variable temperature viscometry. Over an extended temperature range, a plot of ln η *vs.* 1/T is curved, but in the range 10-70 °C all of the liquids follow approximately Arrhenius behaviour (see Figure 3).

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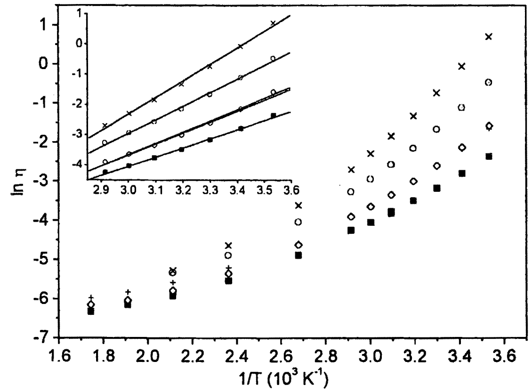

FIGURE 3 Plot of ln η (η measured in Pa.s) against 1/T for [bmim][PF_6] (o), [omim][PF_6] (x), [bmim][Tf_2N] (■), [omim][Tf_2N] (+), and [bmmim][Tf_2N] (◇). Inset shows the same data over the temperature range 10-70 °C with linear fit lines used for calculation of Arrhenius parameters

A comparison of the values of E_a^V and E_a^R for five different ionic liquids is given in Figure 4. This clearly shows that, for a given ionic liquid, effectively identical values are obtained for the activation energies of the energy transfer process and for viscous flow. Thus, the triplet energy transfer process appears to be purely diffusion limited in all of the ionic liquids studied, and the values of k_q obtained should represent limiting values for the rate of reaction of two neutral organic molecules like Bp and Np.

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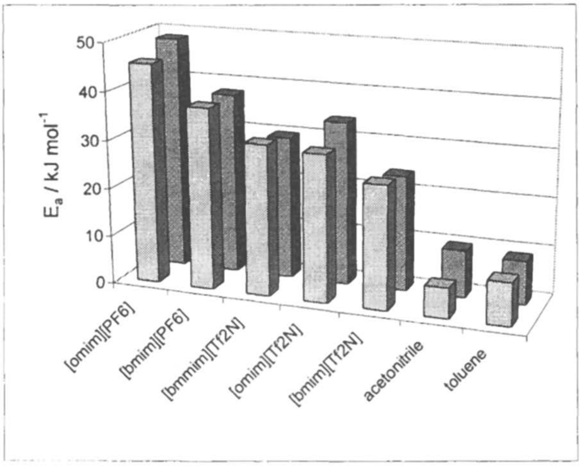


FIGURE 4. Activation energies for viscous flow (E_a^V) (front columns, light grey) compared with activation energies for quenching of ^{3}Bp* phosphorescence by Np (E_a^R) in a range of ionic liquids and conventional solvents.

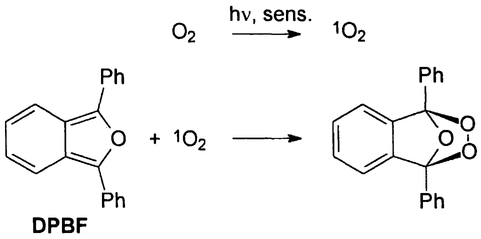
We have used a similar approach to investigate the electron transfer reaction between photoexcited $[Ru(bpy)_3]^{2+}$ ($*R^{2+}$) and the methylviologen dication (MV^{2+}) in ionic liquids (Scheme 2),

$$R2+ \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} *R2+$$

$$*R2+ + MV2+ \rightleftharpoons R3+ + MV^{\bullet +}$$

Scheme 2

and also the photoinitiated Diels-Alder cyclisation reaction between $^1O_2$ and diphenylbenzofuran (DPBF, Scheme 3).



DPBF

Scheme 3

The preliminary results of the former process in [bmim][PF$_6$] have already been reported (*29*). The activation parameters for this process were obtained by monitoring the fluorescence lifetime of $*R^{2+}$ as a function of temperature and $[MV^{2+}]$. For the $^1O_2$/DPBF reaction, it was first necessary to generate $^1O_2$ by irradiation of phenazine in an O_2-saturated ionic liquid. The rate of quenching of $^1O_2$ was then monitored as a function of temperature and [DPBF]. The results gained to date are summarised in Table III.

TABLE III. A summary of kinetic parameters obtained for different reactions in $[bmim][PF_6]$ and $[bmim][Tf_2N]$

Solvent	Reaction	k_q (25°C) / $dm^3\ mol^{-1}\ s^{-1}$	E_a^R / $kJ\ mol^{-1}$	$\Delta S^‡$ / $J\ K^{-1}\ mol^{-1}$
$[bmim][PF_6]$	$^3Bp^* + Np$	1.2×10^8	37.7	28
($E_a^V = 37.6$	$*R^{2+} + MV^{2+}$	2.9×10^7	41.8	29
$kJ\ mol^{-1}$)	$^1O_2 + DPBF$	2.5×10^8	35.5	27
$[bmim][Tf_2N]$	$^3Bp^* + Np$	3.8×10^8	23.9	-9
($E_a^V = 25.4$	$*R^{2+} + MV^{2+}$	1.2×10^8	26.2	-11
$kJ\ mol^{-1}$)	$^1O_2 + DPBF$	5.1×10^8	-	-

Inspection of Table III shows that the activation energies for all three bimolecular processes are very close to those obtained for viscous flow in the two solvents, suggesting that the reactions are basically diffusion controlled in all cases. The largest discrepancy is observed for the reaction between $*R^{2+}$ and MV^{2+} in $[bmim][PF_6]$, but even here E_a^R is higher than E_a^V by only 4.2 kJ mol^{-1}. This suggests that the ionic liquids provide a large degree of charge shielding when bringing together two charged species, with electrostatic repulsions contributing no more than 10 % of the overall activation energy.

For a given solvent, the values of $\Delta S^‡$ are remarkably similar for all processes, even allowing for the large potential errors resulting from the extrapolation required to calculate this parameter. This suggests that solvent reorganisation plays a major role in formation of the transition state, as one might expect from a diffusion limited process. The largest differences between the different reactions are observed in the values of k_q, as one might expect. The electron transfer reaction between $*R^{2+}$ and MV^{2+} is predictably the slowest, as it involves the movement of two large species. As these and other reactions are studied in more solvents, it should be possible to build a picture of how factors such as charge and solute size affect the way that ionic liquids solvate different types of molecule, and the effect of the solvation on the reaction dynamics.

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Summary

The area of photochemistry in ionic liquids remains very incompletely understood. Although the limited range of investigations using solvatochromic dyes are beginning to give a picture of the way in which these solvents interact with different solutes, the level of understanding remains incomplete. Further photophysical studies will hopefully provide more information. The laser flash photolysis experiments have shown that many bimolecular reactions become diffusion controlled in these solvents owing to their large viscosities, even when charge effects might be expected to have large effects. The bimolecular rate constants gained for the different types of reactions should therefore give an idea of the limiting rate constants for different types of chemical reaction. The observation that H-abstraction by $^3Bp^*$ is slower in the $[Rmim]^+$ ionic liquids than in conventional solvents suggests that preparative reactions involving biradical intermediates may provide interesting results. It is clear that many more systems must be investigated, however, if we are to fully understand the properties of these novel solvents.

Experimental details

The ionic liquids were prepared largely following literature procedures, by quaternisation of 1-methylimidazole or 1,2-dimethylimidazole with the appropriate 1-chloro- or 1-bromoalkane, followed by anion exchange using HPF_6, $Li(Tf_2N)$ or NH_4BF_4 as appropriate (*7*, *30*). A number of precautions were necessary, however, to ensure that the solvents were colourless and suitable for spectroscopic and photochemical studies. The 1-haloalkanes were first cleaned following a literature procedure (*31*). This involved washing with concentrated sulfuric acid until the washings were colourless, next with sodium hydrogen carbonate solution, and finally with deionised water to remove the remaining acid. They were then distilled from P_2O_5 immediately prior to use. 1-Methylimidazole and 1,2-dimethylimidazole were vacuum distilled from NaOH immediately prior to use. The quaternisation reaction was carried out either with neat reagents, or with a small amount of anhydrous ethyl acetate added. The reaction was heated at no more than 100 °C under N_2 until the reaction had gone to completion (usually 24 hours for 1-bromoalkanes and 72 hours for 1-chloroalkanes). The ethyl acetate layer was decanted off, and the salt was then dried under high vacuum at 70 °C for several hours.

The water immiscible salts were then prepared simply by mixing aqueous solutions of the appropriate halide salt with a slight excess of HPF_6 (care must be taken as this reaction is very exothermic and HF is generated) or $LiTf_2N$ as appropriate. The ionic liquids separated as dense lower fractions. These were

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then washed repeatedly with deionised water until the washings were neutral, and no trace of halide could be detected. The $[BF_4]^-$ salts were prepared by mixing aqueous halide salt solutions with NH_4BF_4. The resulting $[Rmim][BF_4]$ was then separated by washing with CH_2Cl_2. Careful washing of the CH_2Cl_2 solution with cold deionised water allowed removal of most remaining halide anions, as determined using $AgNO_3$ solution. Unfortunately, the water wash generally also resulted in a decrease in the final yield of $[Rmim][BF_4]$ owing to the relatively high solubility of these salts in water.

All ionic liquids were dried thoroughly by heating under high vacuum at 70 °C for several hours before use. In addition, the solutions used for the solvent probe measurements were dried again in this fashion after addition of the probe molecule. For the flash photolysis measurements, stock solutions of Bp, R^{2+} and phenazine were prepared. Aliquots of the appropriate quenchers were then added to 3 ml samples of the stock solutions to prepare individual samples.

The flash photolysis apparatus consisted of a Nd-YAG laser for excitation operating at 355 nm, and the probe beam was a pulsed Xe arc lamp. The sample was contained in the thermostatted fluorescence cell, and was degassed with dry N_2 (or saturated with O_2 in the case of the Diels-Alder reaction) prior to all measurements. The desired wavelength of fluorescence or absorbance signals were selected using a monochromator prior to reaching the detector. The data were then stored on an oscilloscope, and subsequently transferred to a computer for analysis. Viscometry measurements were carried out using a cone and plate viscometer, with samples again dried as described above.

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Chapter 34

Green Industrial Applications of Ionic Liquids: Technology Review

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During the American Chemical Society National meeting in San Diego, April 1-5, 2001, scientists and engineers from academia, industry, and government research laboratories met for a symposium to discuss *Green (or Greener) Industrial Applications of Ionic Liquids*. The symposium was very successful, with excellent attendance and participation, and generated significant interest from the media, reflected by an article covering the meeting in the New York *Times*, and a follow-up on-line educational supplement.

Towards the end of the weeklong symposium, an evening special Technology Review Session was held, sponsored by the Department of the Army, Army Research Office. The objective of this special session was to review the status and promise of ionic liquids (ILs) for a wide range of new, improved, or more environmentally benign chemical technologies in catalysis, synthesis, separations, and electrochemistry, particularly with relevance to Department of Defense (DoD) issues. The goals of the technology review were to provide a critical assessment of current knowledge in the field, to identify the promise of ionic liquids for the future and to identify key DoD needs for improved technologies that could benefit from applied IL research and development.

Structure and Organization of the Review Session

The Technology Review session was organized around an invited panel of scientists active within the ILs field who were asked to present an assessment of the state-of-the-art on a range of topics from an ILs perspective. The panel was asked to assess critically current state-of-the-art and technical challenges in specific R&D areas (in terms of the current knowledge of physical and chemical properties and applications in synthesis, separations, and materials science) and to identify potential future uses of ILs in Green Technology. Where possible and appropriate, comparisons with other 'neoteric' solvents (e.g., water, sc-CO_2) were made in order to help focus the review on potential applications for environmentally benign technologies.

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Review Panel Participants and Overview Topics

The review topics and leading experts included the following:

- **Ionic Liquids in the Context of Green Chemistry**
  R. D. Rogers (The University of Alabama, USA), K. R. Seddon (The Queen's University of Belfast, United Kingdom)
- **Department of Defense Interests**
  S. Lee (Army Office of Research, USA), P. Trulove (Air Force Office of Scientific Research, USA)
- **Structure and New Ionic Liquids**
  C. M. Gordon (University of Strathclyde, United Kingdom), J. D. Holbrey (The University of Alabama, USA)
- **Separations and Engineering**
  K. N. Marsh (University of Canterbury, New Zealand), R. D. Noble (University of Colorado, USA), W. Tumas (Los Alamos National Laboratory, USA)
- **Electrochemistry**
  J. S. Wilkes (Air Force Academy, USA)
- **Renewable Resources**
  L. Moens (National Renewable Energy Laboratory, USA)
- **Nuclear Applications**
  S. Dai (Oak Ridge National Laboratory, USA)
- **Polymerization**
  J. W. Mays (University of Alabama at Birmingham, USA)
- **Issues in Catalysis and Chemical Synthesis**
  P. Wasserscheid, (RTWH-Aachen, Germany), J. H. Davis, Jr. (University of South Alabama, USA), T. Welton (Imperial College, United Kingdom)

Session Review

The Technology Review was conducted through a series of short presentations from the Panel participants. Each presentation was used as an opening for discussion with participants and attendees. The panel reviewed the current state of IL knowledge; drawing from examples presented in the symposium. Current and potential applications of ILs in technological processes were discussed and both existing barriers to implementation and future requirements in R&D were identified.

Green Chemistry and Ionic Liquids

The technology review was opened by Rogers (Alabama), who discussed outcomes from an earlier NATO ionic liquid workshop (Rogers, R. D. *Green Chem.* **2000**, 2, G93) and recommendations arising from that meeting. Of primary importance, the need for well-characterized, freely available ILs was identified. The need to protect intellectual property was discussed with respect to protecting and controlling accessibility to ILs as states of matter and as process components. Rogers described how the variety of research areas in which IL technologies have been applied has grown recently but is still rather conservative and could benefit from expansion. Similarly, encouragement is needed for more scientists in different disciplines to consider working with ILs on a routine basis. However, in order to enable these goals, a significant educational aspect to the field is needed.

Included in the educational aspect is the training and informing of researcher about the scope, potential, *AND* pitfalls of ILs, most importantly that ILs can be utilized as much more than just non-volatile solvents. As part of the wider educational component, there is need for an IL brochure to help publicize and introduce IL research to a wider audience, including potential funding sources. Discussions following included ways in which industrial, academic, and government R&D groups could work together more closely to develop greener technologies.

Department of Defense Research and Programs

Lee (Army Research Office) and Trulove (Air Force Office of Scientific Research) presented overviews of some of the scientific challenges faced in maintaining and providing new technologies for DoD missions. The role of the Army Research Office in identifying and supporting scientific and technological research in response to the changing operational needs and requirements of the Army was described by Lee.

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Twin aspects of DoD research and technology development were indicated: (i) development of new materials in line with Army needs, including new membranes, materials, barriers, and composites for protection, detection, and decontamination, and (ii) methods to facilitate production of these materials with a drive to weight reduction, facilitating and enabling production of new, low mass, high efficiency systems. Among focal points used as examples were new and improved fuel cells and compact power sources. The Army Research Office supports programs for the study of elastomers, electrochemistry, oxidation, organized assemblies, surfaces and catalysis, fast reaction kinetics, and novel molecules. Aspects of ILs (or other research) for the development of new improved, efficient, clean, high through-put, quick to completion, chemical processes for reactions, polymer production, generation of ceramics, and other matrix materials, etc., in clean-up, separations, and remediation tasks are required. The second aspect includes production of new devices that use IL materials in construction or operation, such as in battery and electrolyte technology, electro- and chemico-active membranes, sensors, etc. Lee suggested, or hoped, he would discover that ILs could be used as new materials, or in improved synthetic and production methods to realize new materials.

Trulove then described the Air Force interest in compact power sources, surface chemistry, electrochemistry, tribology, and corrosion, for applications in aircraft, satellites, and unmanned vehicles. The development of IL electrolytes for power source and electrochemical applications was reported as well established; IL gel electrolytes can be used to prepare novel electrochemical cells. It was pointed out that the long-term AF strategic refueling airframe (in-flight refueling) will be based around the same aircraft in 2040 as in 1960; corrosion protection and remediation treatments, and electrodeposition of aluminum alloys, are important areas of interest.

Structure and Ionic Liquid Properties

The importance of collecting good, well-defined fundamental physical and rheological data on series of ILs and, most importantly, in providing details of purity was considered by Holbrey (Alabama) and Gordon (Strathclyde). It was emphasized that IL properties depend on functionality and interactions between the cations and anions present. In order to understand molecular level interactions as the basis for controlling bulk and solvent-solute properties, complete data sets are needed. Among data required are melting/freezing/glass points, viscosity, density, refractive index, conductivity, diffusion coefficients, etc., in each case collected from well-characterized ILs. Part of an educational component could be teaching researchers about the sort of data needed and desirable to collect. Gordon stated that photochemistry has been shown as a valuable tool for investigating physical and structural aspects of solvent/solute

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interactions, and he believed that sufficient data exists to attempt QSAR models of IL properties.

Tumas (Los Alamos) pointed out that very careful measurements need to be made to understand properties, especially how species interact. Wilkes (Air Force Academy) noted that QSAR is based on the principle that function follows form, and he noted that the most important forces in ILs will not be those forming covalent bonds, but will encompass polarity, hydrogen bonding, and directional charge-charge interactions. More complex statistical modeling approaches, with associated larger data sets, may be required. Chemists and engineers often require slightly different data; however, for both disciplines, the data are not systematically available yet for ILs. Marsh (Canterbury) continued the discussion, emphasizing that a database of available, characterized data would be a valuable asset.

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Separations and Engineering

Noble (Colorado) described engineering unit operations (using volume, concentration, reaction improvements) for solvent extraction, membranes, phase change devices, electrochemistry, microfluids, sensors, and materials synthesis. It was emphasized that the data needed to perform engineering calculations and designs based on IL systems were no different than those required for traditional systems, namely thermodynamic and transport properties, materials compatibility, health, safety, and environmental fate information, and on-line and process analytical measurement techniques.

It was stated that as a community, IL researchers need to gain a better understanding of structural aspects of ILs in order to design improved system performance. Experimental data is needed (above), and predictive methods, based on computational chemistry, should be developed.

Among the opportunities offered by ILs from an engineering and separations standpoint is the ability to modify ILs to obtain specific chemical interactions. This provides a means to enable 'active' ILs, for example by functionalization, mixing, or doping. New solvent systems can allow development of newer processing solutions; for example, ILs can be used as liquid membranes for separations and partitioning, or they can be mounted on solid matrices as supported IL membranes. This process can allow smaller volumes of (expensive) ILs to be used with increased overall surface areas for increased contacting efficiencies.

Exploitation of these characteristics may lead to applications in phase-change precipitation/separations processes, microfluid separations, sensors, gas and metal separations, and as catalyst hosts. Separations, recovery, and cleaning of ILs and matrices, however, need to be addressed.

Discussion was based on engineering operations and separations. Questions were raised concerning how to clean ILs and how to extract/remove reaction byproducts, in particular salts, and many answers referred to 'non-classical approaches; Davis (South Alabama) pointed out that in an 'ideal' atom efficient process, there is no waste stream and that we should not necessarily be restricted to using conventional cleaning processes. Success combining ILs with supercritical fluids has demonstrated this. Using ILs just as nonvolatile replacements for organic solvents does not necessarily lead to a green or improved reaction or process.

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Electrochemistry and Energy Applications

Wilkes (Air Force Academy) began by stating that ILs have some prospects for technological applications relevant to military operations, energy generation, and storage, and he addressed environmental concerns. He noted that USAF requirements for improved battery technology jump-started ILs research and that there are still significant improvements that can be made in electrochemical applications and in energy generation and storage. Future electrolyte candidates will require high conductivity, wide electrochemical windows, high thermal stability, high transport numbers, and low flammability, toxicity, and cost.

Environmental benefits from using thermal fluid heat storage devices for solar energy utilization were examined taking advantage of the wide thermal range, low volatility, high heat capacity, and high latent heat of fusion of some ILs. Wilkes also showed that electrodeposition of alloys, especially aluminum alloys, is another useful niche for IL electrolytes. In the case of aluminum alloys, the chloroaluminate ILs were cited as the best because they contain a high concentration of reducible Al(III). Wilkes reported that to date Co, Cr, Cu, Fe, Mn, Ni, and Ag have been alloyed with aluminum from low temperature ILs.

Biomass and Renewable Resources

Concepts for using ILs in biomass processing for creation of new materials and feedstocks were discussed by Moens (National Renewable Energy Laboratory). The use of biomass as a raw material for the chemical industry is important from an environmental and economical perspective; however, biomass raw materials are complex composites in both structural and chemical composition, and require a completely new set of technologies and protocols for their processing into well-defined molecular fractions. Moens suggested that the use of ionic solvents for processing these challenging materials could potentially lead to unique new products, for example novel low weight, high strength biopolymers. The impact on material science could, therefore, be significant.

Moens reported that preliminary work at NREL has shown that the unique chemical characteristics of ILs lend themselves well to chemistry with sugars and promise to deliver alternative processing routes to valuable carbon sources for new chemicals and materials. Opportunities for innovation were described using hydrolysis under acidic or basic conditions to convert polysaccharides such as cellulose to glucose and smaller molecules. Polyols or dicarboxylic acids production from sugars was highlighted as a desirable target for formation of useful monomers.

The acylation of sugars could open up the possibility of condensing polyfunctional molecules that would generate polymeric structures. Unique solubility characteristics of ILs could thus enable production of polymers with high molecular weights.

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Nuclear and Materials Applications

Dai (Oak Ridge) discussed use of ILs as solvents to prepare nanomaterials, and in nuclear separations. It was stated that although electrodeposition from ILs is well established, the challenge is to develop high-quality coherent coatings, which require high conducting, low viscosity media. Dai suggested that new highly conducting, low viscosity ILs with a large electrochemical window should have a profound effect on new electroplating technology, fuel cells, and double layer capacitors. Dai reported the development of an ambient temperature process for synthesizing high quality aerogels using ILs as solvents and the synthesis of composite materials made of ILs and organic or inorganic polymers. These new materials may give rise to novel solid-state supports for catalytic reactions or separation.

Uses of ILs in nuclear processing as low volume replacement solvents for organics in solvent extraction were highlighted. ILs appear to offer the potential for increased concentration of waste streams by enhancing distribution ratios. The use of selective ligands for enhancement of separation efficiency for fission products has been investigated. High separation efficiencies have been observed for actinides and some transition metal ions. The future research in this area may also include the investigation of electrowinning and electrorefining for actinide species in ILs, which could yield unique separation processes for actinides from rare earth fission products.

Dai discussed several issues that need to be resolved to develop practical applications. These included (a) reduction of loss for ILs, (b) recycling of expensive ligands and ILs, (c) radiation stability, and (d) extraction mechanisms.

Polymerization Technologies

Mays (Alabama-Birmingham) reported that new polymerization technologies utilizing ILs as polymerization solvents have recently emerged. In radical polymerization reactions, marked improvements over conventional solvents have been observed, yielding high MW polymers (order of magnitude higher than conventional), narrower polydispersities, rapid rates of polymerization, and convenient isolation of products. Radical copolymerization in IL solvents has allowed block copolymers to be synthesized by sequential monomer addition using conventional initiators (e.g., 2,2'-azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO).

Mays explained that ILs appear to be excellent solvents for radical polymerizations, enabling long radical lifetimes and the formation of high MW, low polydispersed polymers, however, results are still preliminary. Obstacles to success appear to be relative ignorance of polymer scientists of ILs, leading to a lack of research and resultant isolation of research groups. Increased cooperation between experts in polymer science and experts in ILs is likely to yield significant developments leading to green polymerization processes, new polymers, and reduced production costs. Comments indicated that commercial success is possible but will require cost and economic assessments, and regulatory issues will be important. Potential uses of ILs as plasticizers, etc., will also require the same toxicological and regulatory information. Mays considered this data to be of vital importance, especially when issues in polymer science regarding polyvinyl chloride and phthalate plasticizers are considered.

Challenges in Synthesis and Catalysis in Ionic Liquids

Welton (Imperial College) described one of the significant current limitations in ILs research: that, in most cases, the fundamental understanding of the characteristics and solvent properties of IL systems is absent. Welton felt that this was the most significant limitation to advances in the field, stating that without an understanding of ILs, it is not feasible to attempt to design a new process using ILs with the expectation of improving on existing technology.

This theme was continued by Wasserscheid (Aachen), who expanded on the need for high availability, well characterized, IL systems. The evolution of IL science and the types of ILs used will inevitably lead to changes; development of new air/water stable ILs has expanded science, and we can expect this to continue. Cost and purity issues need to be addressed.

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Closing Remarks

The Technology Review session was closed by Seddon (The Queen's University of Belfast), who emphasized that some of the greatest obstacles to current use of IL processes are the lack of data and studies on toxicological and environmental fate. Chemistry is not the obstacle; it is a challenge, whereas addressing how to destroy an IL, what components (cation, anion, or combinations) may in time be problematic, toxicological and biological issues, and ultimate fate is unglamorous but a major concern. Chemists and chemical engineers may not be best equipped to tackle these issues and expertise from other disciplines must be introduced in order to expand the skills base within the IL community.

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Outcomes and Recommendations

The review and subsequent discussions highlighted a number of important general features. The application of ILs to green technological challenges is a new and rapidly developing area. The underpinning technological and scientific understanding of ILs and the paradigm shift changes required in successfully using ILs are not well understood and require extensive education, training, and collaboration across scientific disciplines.

Old habits die hard and have been carried over into ILs research. Examples include claims that replacing a VOC as reaction solvent with an IL leads to a green process, or that it is green to use an IL reaction solvent and then use VOCs for product separation. The goals of green chemistry should drive investigations: ILs can only be used as direct solvent replacements for VOCs in green applications when significant overall improvements in reaction efficiencies are observed. In many literature examples, this is not the case, and ILs offer no advantages over other traditional solvents. However, studies of many organic reactions, such as the Diels-Alder, Suzuki, and Friedel-Crafts reactions, suggest that for many reactions, IL solvents may give rise to superior results in terms of yield of reaction, product selectivity, and ease of isolation. Such findings are of potentially significant environmental and commercial importance.

The aim of the Technology Review was to assess the current state of knowledge in ILs science and technology, and to identify areas in which a target program of ILs R&D could be anticipated to bring about significant improvements over current practices and research requirements for future development and successful utilization of IL technologies. These outcomes are summarized below:

- IL purity is a significant factor in influencing physical properties and reproducibility of results. Information on purity and contaminants (especially water content, organic and inorganic impurities, etc.) is crucial for characterization and comparison of results and process design.

- A concerted effort needs to be made to establish structure-property correlations for ILs; these will largely derive from studies of the physical properties of the salts, especially properties such as melting points, glass transition temperatures, gas solubility, and viscosity. Consequently, one element of this effort should include the establishment of a publicly accessible database of reliable physical property data on ILs.

- The scope of applications taking advantage of ILs needs to be expanded, especially to extend beyond the use of ILs just as non-volatile solvents – exchanging a volatile organic solvent for an IL solvent does not necessarily make a green process. The broad, growing effort to investigate the full range of reaction chemistry and synthesis in ILs should be sustained.

- ILs can be used as components for integration into device technology. Potential examples include coating, sensors, membranes, IL-impregnated membranes as conductive barriers for fuel cells, etc.

- New ILs should be prepared and evaluated. It is clear from work done so far in the evolution of this infant field that the solvation capacities of ILs can be altered by changes in the composition of the ions from which they are composed. Energetic efforts thus need to be made to design ILs optimized or tailored to specific applications. The validity of this concept has already been established for certain reactions and separations processes, using so-called "task-specific" ILs.

- Modeling studies may be the key to understanding ILs in terms of anion and cation identity. A fundamental understanding is needed in order to enable accurate prediction of properties in macroscopic modeling (e.g., thermodynamics, rheology), as well as microscopic and quantum mechanical modeling (e.g., ion conformations and interactions in a liquid environment). Modeling requires reliable, well-characterized empirical data for comparison.

- Intellectual property regarding ILs should be treated in a manner that allows the continued development of IL technology and applications. The onus is on intellectual property holders to encourage and facilitate exploratory research.

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- Toxicity data, including personal, environmental, and safety aspects is required. Protocols for evaluating the toxicological properties of new ILs need to be developed in conjunction with regulatory authorities (e.g., EPA, FDA, etc.)

Conclusions and Questionnaire Responses

A questionnaire was prepared for participants and attendees of the Technology Review session in order to gather feed-back on the session. The questionnaire was comprised of six questions or points that were intended to elicit a response from the audience. Thirty-seven completed forms were collected at the end of the session.

The questions and a general assessment of the responses to each question are given below. The diversity of interests and experience in the field, present for the review was self-evident.

1. *What was achieved at the Technology Review Session?*

   There was a good discussion, defining the current state of IL science and technology with communication between chemists and engineers. The review benefited from fairly open disclosures from the speakers, and while nothing was given away, the areas that could benefit from IL applications were well covered with a good exchange of data. However, some participants reflected that the level of discussion was at the lowest common denominator, and that the (closed) NATO ARW meeting in Crete was more focussed – this may have been a result of the higher level of industrial participation in that meeting.

2. *What do you feel is the current state of knowledge concerning ILs technology and applications?*

   Many respondents felt that the field was in a formative, but rapidly growing period. 'Infancy' was used on a number of occasions, however, other comments indicated a feeling that knowledge was fairly advanced in terms of reaction mechanisms and appears to be moving towards industrial applications, however, the rush towards IL applications leaves many gaps in understanding the fundamental parameters that define ILs. It was felt that these need to be addressed to enable 'scientific' progress. One participant commented that there seems to be a real lack of depth of knowledge *within* the present community about the existing literature on ionic liquids, especially work on chloroaluminates.

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3. *Identify the barriers to successful utilization of ILs.*

   Lack of available basic data on IL systems was identified in many responses as the major barrier to application. Areas noted included information on mixtures, toxicity, recycling, separations, properties of state, structure and dynamics on the microscopic scale, and legal aspects from IP restrictions to utilizing ILs in basic research. Potential commercial cost and availability of ILs were also considered to be major problems, as was the absence of life-cycle assessment, biological fate, and toxicological data.

4. *In what areas could ionic liquids be used in place of existing processes or materials? What are the real and/or perceived advantages from using an ILs process?*

   Suggested application areas given included replacing undesirable aprotic solvents in chemical reactions with advantages to be gained from changes in reaction characteristics, in solvent extraction (of organics, metal ions, and complexes), advanced materials synthesis, optoelectronics, magnetic materials, ion selective electrodes and sensors, selective absorption and complexation media, electrochemistry and electrosynthesis, and low temperature metal refining (with lower overhead operating costs). Some respondents felt that the meeting did a poor job of addressing these aims, that there were no convincing potential applications of ILs, and that ILs were just a novelty. One participant remarked that ILs are just liquids with a certain set of properties (which include wide liquid range, low vapor pressure, electrically conduction, and ionic nature) and so could be used in just about any application, while another respondent considered that, while replacing current solvents was a reasonable first step, 'metal bridges are not made like stone bridges,' and these novel liquids offer opportunities to develop new, novel processing methodologies.

5. *What R&D needs to be done in the future? Can you identify effective goals for both short and long-term research and development, in order to implement ILs processes with identifiable benefits?*

   The bulk of responses considered that there are only limited comprehensive studies on ILs. Complete thermodynamic characterization and a coherent database of information are needed in order to achieve predictive capabilities. The current ability to achieve knowledge transfer is poor, more educational material is needed. Industrial needs and scale-up methodologies should be identified, as should potential applications and materials uses of ILs beyond replacements for volatile organic solvents. Toxicological, environmental fate, and life cycle assessment and economic impact studies are needed. It was also suggested that interdisciplinary team approaches, demonstrations of 'promising' technologies, electrosynthesis applications, and a wider variety of hydrophobic (or water resistant) ionic liquids appear to be desirable.

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6. ***What opportunities and areas could ionic liquids be used for in the future that we have not yet envisaged?***

   Many respondents wished to keep their ideas for future developments to themselves, at least until initial findings could be reported. However, a wide range of generic topics were suggested. Surprisingly, while most current literature (and the content of symposium presentations) describes uses of ILs as solvents for reactive chemistry, most suggestions for new uses were firmly in a materials chemistry field. Suggestions included lubricants, sensors, nuclear waste reprocessing (metal separations), polymerization and gellation of ILs, incorporation into mesoscopic materials, microfluidic processes, continuous rather than batch synthesis processes, electrochemical synthesis, using metallate ionic liquids in catalysis, and life-science studies on viral and enzymatic processes.

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Summary

As yet, ILs-based processes or technologies have not reached large-scale commercial application, though there are a number of good candidates. It is however, naive to expect that this should take place overnight. The timescale from invention to implementation may be large and screening and development is necessary before investing in full-scale commercial programs.

ILs have been established as useful solvents and liquid materials for chemical reactions, separations, and electrolytes and are clearly much more than scientific curiosities, though they have many curious properties. ILs research is relatively immature and has been, to date, relatively specialized, primarily in electrochemistry. However, a significant body of data is available especially from the electrochemical literature that needs to be taken on board – using ILs as solvents for 'green' or otherwise chemical applications is a new area and the researchers require education. In likening the current position to that of sc-CO_2 ten years ago, one comment in the questionnaires correctly reflects the state of knowledge. However, ten years ago, sc-CO_2 applications and systems had been actively studies for over 150 years, and the introduction of new, green sc-CO_2 techniques into the industrial mainstream is only now beginning.

As the field comes to maturity, the degree of innovation against time will follow an S-shaped curve, familiar to technological development. We are currently only at the bottom of the curve, with the expectation of many new developments and applications to come.

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